

**TNO Automotive**

**TNO report**

**93.OR.VM.029/1/PHE/RR**

**Regulated and unregulated exhaust gas  
components from LD vehicles on Petrol, Diesel,  
LPG and CNG**

363/08<sup>P</sup>

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93.OR.VM.029/1/PHE/RR  
(Projectnr. 733150002)

REGULATED AND UNREGULATED EXHAUST GAS COMPONENTS FROM LD VEHICLES ON PETROL, DIESEL, LPG AND CNG

Authors

Number of Pages  
95

Number of Appendices  
-

Number of Figures  
37

Number of Photographs  
-

Number of Tables  
31

Client/Sponsor

- Ministry of Public Housing, Physical Planning and Environment
- Ministry of Transport, Public Works and Water Management
- Stichting RESAP
- Koltec B.V.
- Necam B.V.
- Vialle Autogas Systemen B.V.
- IW-TNO

Date

26 October 1993

Initiated by

Approved by

Also seen by

Also seen by

Research period

week 45-91 to 52-92

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## Preface

Since the introduction of the exhaust gas legislation in the early seventies much has been attained with regard to the reduction of exhaust emissions of passenger cars. Originally the emphasis lay on the emissions of carbon monoxide and hydrocarbons, that had been decreased to about 30-35% of their original values in the late eighties in the case of petrol engined cars. Introduction of the catalyst has reduced these values further to about 5-6% of the original values. The emissions of oxides of nitrogen, with which until then little had been attained, has now been reduced to about 13% of the original value. And all of this with a fuel consumption (important because of carbon dioxide emissions) that decreased by 25%.

In the mean time our basis of judgement has shifted as well, however. An unparalleled increase in the number of vehicles counteracted the reduction of the total national emission numbers, and smaller absolute differences in emissions have become more important now than 25 years ago. At the same time the number of exhaust gas components in which we are interested has increased. That means that mutual differences in emission for different fuels, which have decreased significantly in an absolute sense, but are still present in a relative sense, can still be of importance or become again important.

So the question which fuel or which mix of relevant fuels should be preferred from an environmental point of view is still as relevant today, as it was 25 years ago. In 1992 this question has been viewed with the use of a studymodel, in which the expected emission behaviour for 2010 was calculated for a number of possible variants in the fuelmix. Primary interest lay in the known, regulated components. In the present study the same question has been viewed on the basis of an extensive measurement programme, in which primary interest went to a large number of unregulated components. This programme too was set up in a future-oriented way as much as possible.

From both studies it can be concluded that gaseous fuels (in practice that will mean mainly LPG) can still contribute to a further reduction of traffic emissions, even in this time of low absolute emissions, and that it would be countereffective when LPG would disappear from the market, or become less attractive to the business driver. That this fact is relevant for future policymaking goes without saying.

## Summary

In the project reported here four fuels - petrol, LPG, CNG and diesel - are compared on passenger cars and light vans. The comparisons are made for the usual regulated components, but also for a number of unregulated components. The project was financed by the Dutch government, the association of gas suppliers, a number of LPG/CNG equipment manufacturers, and TNO. The measurements were performed by IW-TNO and IMW-TNO. See further chapter 1.

For each fuel four passenger cars and one light van were selected, except for CNG where only one passenger car and one light van were chosen. The vehicles were selected to represent the most modern technology; they were all relatively new. The fuel specifications represented those to be expected in the near future, especially with regard to sulfur content. The components measured were:

- \* CO, HC and NO<sub>x</sub>;
- \* NO<sub>2</sub> and CO<sub>2</sub>;
- \* aldehydes (15 different components);
- \* polynuclear aromatic hydrocarbons (PAH, 22 different components);
- \* C<sub>1</sub> to C<sub>12</sub> hydrocarbon speciation (40 different components);
- \* to a limited extent: nitro PAH

The measurements were taken over a number of different driving cycles, some of them starting from cold (see further chapter 2).

A short summary of the sampling and analysis is given in chapter 3. A more detailed discussion is given in a separate report.

With regard to the regulated components, petrol scores highest on CO for all cycles, followed by LPG. The HC-emission is highest for the CNG-vehicles; this HC is mainly methane which is not much affected by the vehicle's catalyst. The diesel engine is noteworthy for its relatively high emission of NO<sub>x</sub> and particulates. The amount of NO<sub>2</sub>, as a part of NO<sub>x</sub> varies from 6% for CNG via 11% for petrol and LPG to 25-30% for diesel engines. Since the NO<sub>x</sub>-emission is highest for diesel engines already, the diesel clearly scores highest in NO<sub>2</sub>. With regard to CO<sub>2</sub> petrol always scores highest and CNG usually lowest; LPG and diesel usually are of the same order. The other unregulated components show a great mass of data that cannot be summarised in a few words. All these data are shown in the separate data-report and in a summarised way in chapter 4.

In order to draw some broad trends through the data, a number of environmental effects has been defined and the contributions of the measured components to these effects have been calculated. The background to this approach is given in detail in a separate report. The effects considered are:

- \* Direct toxic and nuisance effects  
CO, NO<sub>2</sub>, particulates, lower aldehydes
- \* Long-term toxic effects  
PAH, BTX (benzene, toluene, xylene), lower aldehydes
- \* Summersmog potential  
reactivity defined as ethene-equivalent: C<sub>1</sub>-C<sub>12</sub>, aldehydes, CO and NO<sub>x</sub>
- \* Wintersmog potential  
related to total particulates emission
- \* Acidifying potential  
acid equivalent expressed as mmolH<sup>+</sup>: NO<sub>x</sub> and SO<sub>2</sub>
- \* Global warming potential (GWP)  
expressed as CO<sub>2</sub>-equivalent: CO<sub>2</sub>, CO, CH<sub>4</sub>, NMHC and NO<sub>x</sub>

The direct toxic effects are considered at a local scale. The other effects have been calculated over a weighted average of all driving conditions. A qualitative evaluation of all effects is shown in Table 1. See further chapter 5.

Since some cycles were measured both in coldstart and in hotstart condition, it was possible to evaluate the coldstart effect of the various fuels on the different components. In general the catalyst equipped vehicles had a significant coldstart effect on most emissions; the diesel vehicles showed much less coldstart influence. Of the direct toxic components CO showed a large coldstart contribution on petrol and (less) on LPG. The emission of the lower aldehydes showed some coldstart effect on the diesel vehicles. The other components (NO<sub>2</sub> and particulates) are mainly a diesel problem and show no significant coldstart effect on that fuel. Of the long-term toxic effects PAH is mainly a diesel problem and shows no coldstart effect on that fuel, while BTX is mainly a petrol problem and shows a clear coldstart effect on that fuel. For the lower aldehydes: see above. Summersmog, wintersmog and acidification are mainly diesel problems and therefore show no or only a small coldstart effect. The Global warming potential has a coldstart effect of 7-11% for all fuels. See further chapter 6.1.

An estimate was made of the indirect emissions (due to oil production, transport, refining and distribution) and the not-measured effects (such as evaporation or the emission of N<sub>2</sub>O). When these effects are taken into account and the results are compared to the conclusions drawn before, it turns out that CNG is less good on PAH and slightly less good on the lower aldehydes, whereas diesel is less bad on these two components. The effect on BTX is negligible. With regard to wintersmog and acidification CNG shows much better and diesel somewhat less bad. The effects on summersmog are negligible. The relative merits on GWP show small changes, but since the differences are not big anyway the resulting shifts do have some significance. The main effect

is, however, that petrol deteriorates relative to the other fuels. See further chapter 7.

A statistical evaluation shows that of the direct toxic components CO is differing significantly from the other fuels for petrol (higher) or sometimes CNG (lower), NO<sub>2</sub> shows statistical significant relations for most comparisons, as do aldehydes, while the particulate emissions only show a significant difference for diesel engines. Of the long-term toxic components PAH is only significantly different for diesel engines and BTX for petrol engines. The lower aldehydes, as stated above, are significant in almost all cases. Of the regional and global environmental effects wintersmog is related to particulate emission and therefore only significantly different for diesel engines. Summersmog and acidification are significant for most options, as is global warming. The significance tends to increase when indirect effects are taken into account as well. See further chapter 8.1.

Two coldstart tests were measured in duplicate. This allowed the repeatability to be judged. This turns out to be poor at very low levels of emission, but good at higher levels of emission. So the identification for the fuel that emits highest can be made with good repeatability for all emission components. As for the environmental effects: their repeatability is usually better than that of the individual contributing components. Obviously some levelling out takes place. Since the repeatability of hotstart tests is usually better than that of coldstart tests, the repeatability of the testing may be regarded as good. The differences found between the various vehicles on one fuel, which are sometimes substantial, must therefore be regarded as real. See further chapter 8.2.

## CONCLUSIONS

### General:

The first impression on regarding the measured values is that the exhaust gas quality of modern cars has improved very much over that of 20 years ago. That also means that the mutual differences between the various fuels are usually small when taken in an absolute sense. Yet, these same differences may become important again when the total fleet or the national annual kilometrage increases. This is especially valid for the global warming potential, where the differences are much smaller than for other components (since there is no quick way to reduce the emission of CO<sub>2</sub>).

### Catalyst equipped vehicles:

Catalyst equipped vehicles have in principle the disadvantage that the emission reduction is limited during the warm-up periods, when the catalyst



is not, or not fully, active. On average this cancels out against the very low emissions once the catalyst is active (i.e. after the first  $\frac{1}{2}$  to 1 kilometer). But it is an aspect in local circumstances, such as an urban environment, where many coldstarts take place, or in situations where only very short trips are made.

#### Petrol:

This fuel does indeed show a marked coldstart effect which influences the emissions of CO, BTX, the lower aldehydes and PAH (the latter especially in light van operation). Of these the emission of CO is only of relative importance, since with this class of vehicle the absolute values are so low, that there is no real CO-problem in the average urban environment anymore. On the positive side the emission of particulates is better than average in some driving cycles. The global warming potential is the worst, however, of the four fuels.

#### Diesel:

The results on diesel fuel show a high to very high emission of direct toxic components, with the exception of CO. The same is true for the long term toxic effects. The regional and global environmental effects vary from high (wintersmog and acidification) to very high (summersmog). The global warming potential scores average, between petrol and LPG.

#### Gaseous fuels:

The gaseous fuels score better than the liquid fuels on all accounts. The coldstart effect is mainly limited to a slightly elevated CO-emission with LPG, but, as stated above, CO has no great importance considering the absolute levels concerned. When comparing the two fuels CNG often scores better than LPG, although LPG scores better on particulates (and therefore also on wintersmog potential). The feasibility of LPG as a fuel for passenger cars is in practice clearly higher than that of CNG, however.

#### Local circumstances:

With regard to local circumstances it may be noticed that the traffic jam often led to unexpectedly high emissions of most components. In the very first place this has to do with the extremely high fuel consumption per kilometer travelled (because of the low speed; per unit time the fuel consumption is normal). But it also appears that some fuelling systems are obviously not optimised for this stop-and-go patterns. This condition is not part of the official certification procedure.

Table 1: Evaluation of effects (without indirect emission)

Direct toxic and nuisance effects	Petrol	LPG	CNG	Diesel
CO	o	o/+	++	+
NO <sub>2</sub>	o	o	+	--
particulates	o/+	+	o	--/-
lower aldehydes	o	o	+/++	--/-

Long term toxic effects	Petrol	LPG	CNG	Diesel
PAH	o	+	+	-
BTX	-	o	o	o
lower aldehydes	o	o	+	-
summary	-/o	o/+	+	-

Regional and global effects	Petrol	LPG	CNG	Diesel
summersmog	-	o	+	--
wintersmog	o	o/+	o	-
acidification	o	o/+	o/+	-
GWP	-/o	o	o/+	-/o
summary	-/o	o/+	o/+	-

Summary of effects	Petrol	LPG	CNG	Diesel
Dir. Toxic	o	o/+	+/++	--/-
LT Toxic	-/o	o/+	+	-
Reg./global	-/o	o/+	o/+	-

#### RECOMMENDATION

The results of the programme point clearly to a general superiority of gaseous fuels. Of these gaseous fuels LPG is obviously the most feasible, at least on the short term. When one compares LPG with petrol it appears that although LPG scores consistently better than petrol, the differences are nonetheless small in an absolute sense, due to the low absolute level of emissions. However, in practice one will have to compare LPG with diesel fuel. LPG is mainly used by people who drive (much) more than average (and usually for business). For such drivers diesel is the logical alternative. The project has made clear that LPG wins on all accounts from diesel, with the exception of CO in some cycles. This leads to the conclusion that LPG can play an important part in the Dutch car fuelmix, and that it would be a bad thing if LPG would disappear from the scene, or if the attractiveness of LPG for the business driver would shift towards diesel fuel. This conclusion is



in line with that from the study "Change in fuelmix" [7] that was carried out for NOVEM in 1992.

So the programme would lead a.o. to the recommendation that care should be taken to assure that the share of gaseous fuels in the national fuelmix is maintained, if not increased. This is all the more of importance since at the time of writing there is a real danger that LPG will disappear from the market, since the cost/benefit ratio is changing to such an extent that the use of LPG becomes unattractive to the potential user.

In continuation of this project at this moment another project is in progress with the aim to quantify as much as possible the benefits of using LPG as an automotive fuel. A LPG drygas multipoint injection system (the latest generation) is installed in a modern dual fuelled petrol vehicle. Instead of the standard system (as used in this project), now TNO has optimized the vehicle on LPG in cooperation with the car manufacturer and the LPG equipment manufacturer. The LPG vehicle can still be used on a retrofit basis, so it is commercial attractive. With this vehicle the same range of regulated and unregulated components is measured.

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## 1 INTRODUCTION

With the advent of the closed-loop 3-way catalyst for spark ignition engines and the 'environment-diesel' by some manufacturers the question of the relative merit of various fuels with regard to exhaust emission quality has gained a new interest. Such a question can be asked for the global emission situation, but also for a local environment such as a town centre. The question need not be limited to the normal regulated exhaust components, but could be enlarged with other, unregulated components.

In order to provide a well-founded answer to this question, an experimental programme was set up to measure actual emissions of various vehicle-fuel combinations under a range of conditions, however, with an emphasis on the urban environment. This programme was funded by the Dutch government (Ministries of Transport and Environment), the 'Stichting' RESAP (Association of gas suppliers), a number of LPG/CNG equipment manufacturers (Koltec, Necam, Vialle) and TNO. The work was carried out by IW-TNO. IMW-TNO carried out the analyses of the non-regulated exhaust components.

A total of 17 vehicle-fuel combinations was measured over 4 different driving cycles in both coldstart and hotstart situations. The fuels included petrol, diesel, LPG and CNG (Compressed Natural Gas). A range of regulated and non-regulated exhaust components was measured.

The vehicles selected for the programme represented for the major part modern, or where possible even advanced, technology.

Since the programme generated nearly 10,000 individual emission data an attempt has been made to group them together and to classify them according to environmental impact. Such a classification may, of course, be open to criticism, and some may regret that some detail is lost. Yet it seems the only possible way to introduce some order into an otherwise insurmountable mass of data.

### 1.1 The significance of car emissions

In Fig. 1.1 is shown what the contribution of traffic is to the total of man-made emissions in the Netherlands (source: Central Bureau of Statistics). The graph gives the direct emission components as measured. With regard to the environmental effects, referred to above (and explained in detail in chapter 5) the following can be said. The proportion of CO and particulates can be

read directly from the graph. The proportion of  $\text{NO}_2$  can be deducted from the proportion of  $\text{NO}_x$  and the proportion of the lower aldehydes to a certain extent from the proportion of VOC (Volatile Organic Compounds, including aldehydes). The proportion of long-term toxics cannot be deducted from this graph, although the proportion of VOC suggest that it could be significant.

The contribution of traffic to summersmog is related to the proportions of the emissions of VOC, CO and  $\text{NO}_x$ . These proportions are large. The contribution to wintersmog is related to the proportional contribution of particulates and  $\text{SO}_2$ . These proportions are low, especially for light traffic.

The contribution of traffic to acidification is related to the contribution to  $\text{NO}_x$  and  $\text{SO}_2$ . The contribution to  $\text{SO}_2$  is low, especially for light vehicles, but the contribution to  $\text{NO}_x$  is extensive. In the Netherlands  $\text{NO}_x$  contributes for about 20% to acidification; in many other countries this proportion is higher (a.o. because they have a lower  $\text{NH}_3$  impact).

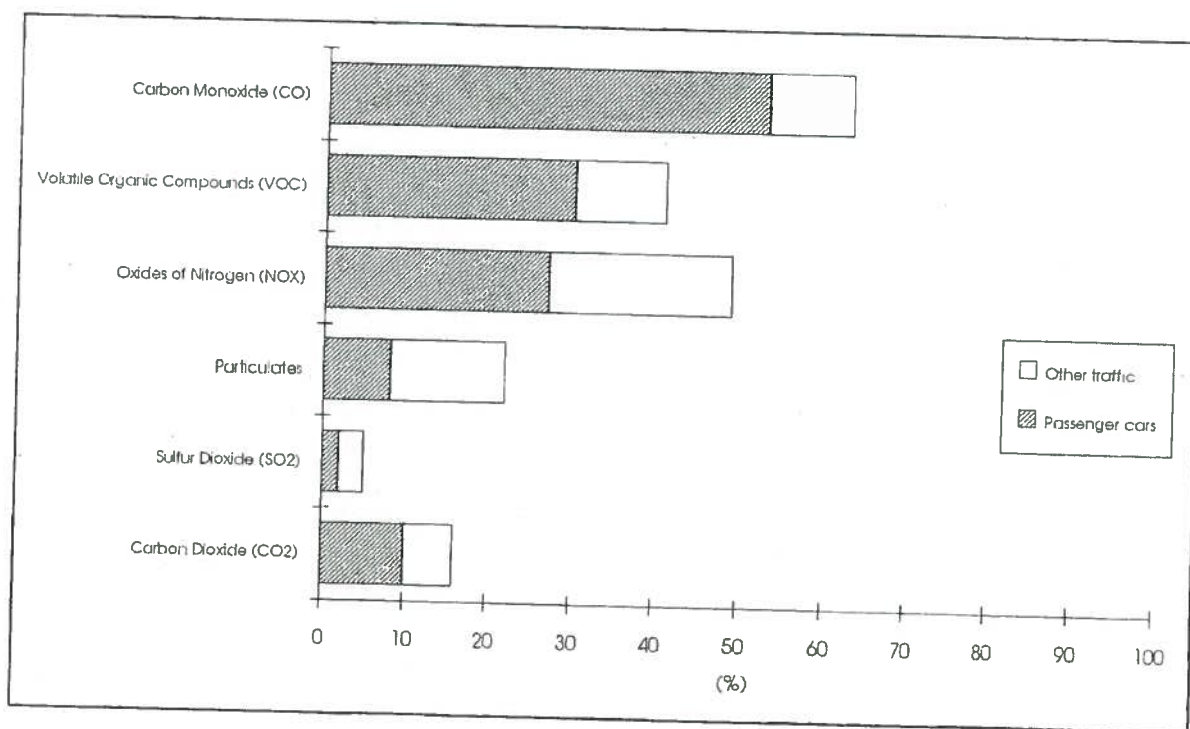


Figure 1.1: Proportion of traffic emission in the man-made emissions in the Netherlands (situation 1990)

## 2 MEASURING PROGRAMME

A total of 17 vehicle-fuel combinations was tested, of which 13 are related to passenger cars and 4 to small vans. To this end 10 actual vehicles were selected (8 cars and 2 vans), of which 5 (4 cars and 1 van) with spark ignition engines and 5 others (also 4 cars and 1 van) with compression ignition engines. The spark ignition engines were all tested on petrol and LPG, while 2 (1 car and 1 van) were also tested on CNG. The full selection is shown in Table 2.1.

In selecting the vehicles care was taken to obtain modern technology including for the spark ignition engines:

- \* 4-valve engines
  - \* multipoint fuel injection
  - \* closed-loop 3-way catalyst
  - \* exhaust gas recirculation (EGR)
  - \* if possible: variable valve timing
- and for the compression ignition engines:

- \* turbocharging
- \* direct injection
- \* electronically controlled injection
- \* EGR
- \* oxidation catalyst

Three petrol vehicles were equipped with a microprocessor controlled closed-loop LPG system, the other two with the new LPG drygas multipoint injection system (the latest generation). The two CNG vehicles were fitted with the last-mentioned system for CNG (the latest generation).

Table 2.1 also shows which vehicles were adapted with which of these features.

The test cycles combined European and American standard procedures with actual driving patterns. The new European testcycle, consisting of urban driving cycle (UDC) plus extraurban driving cycle (EUDC) was driven both in coldstart (coldstart European driving cycle) and in hotstart (warm European driving cycle) condition. The coldstart test was done in duplicate, to improve reproducibility. The American test was the US'75 procedure, that already contains one coldstart and one hotstart. According to the official procedure three phases have to be measured separately and have to be combined according to certain weighting. For cost reasons it was not possible, however, to take three samples of the unregulated components. So only one sample

was taken, that does, for that reason, not fully represent the 'official' US'75 result. Additionally two actual driving patterns (established in actual traffic) were driven. One was a typical urban journey with coldstart (actual urban driving pattern). Again for reproducibility this was driven twice. The other was a typical traffic jam, with stabilised engine (actual traffic jam pattern). Table 2.2 lists all the variants.

The components measured comprised the regulated components (CO, HC, NO<sub>x</sub>, particulates) plus CO<sub>2</sub> and NO<sub>2</sub> (as NO<sub>x</sub>-NO) and a number of unregulated components. The unregulated components fell into the following different groups:

- \* aldehydes (15 different components)
- \* polynuclear aromatic hydrocarbons (PAH, 22 different components)
- \* C<sub>1</sub> - C<sub>8</sub> hydrocarbons (13 different components)
- \* C<sub>9</sub> - C<sub>12</sub> hydrocarbons (27 different components)
- \* nitro-PAH

Of nitro-PAH seven different components were analysed, but only one rose above the detection limit. Also this group of components was only measured on six vehicles, and over the total of all driving cycles in order to get sufficient sample for detection (see Table 2.3). The actual components analysed are shown in the Tables 2.4-2.8. An attempt to also analyse SO<sub>2</sub> was abandoned because no suitable analyser was available.

The fuel used has been commercial fuel. This was obtained in one batch so that all vehicles have been run on the same fuel. For the diesel vehicles a low sulfur fuel has been used (0,03% S) that, also in its other characteristics, may be regarded as a characteristic fuel for 1996 and beyond.



Table 2.1: Vehicle-fuel combinations

SPARK IGNITION ENGINES						
1. Honda Civic 1.6 ESi	petrol	LPG (Landi H.)	CNG (Koltec)			
2. Lancia Thema 2.0 i 16V	petrol	LPG (Necam)				
3. Opel Vectra 1.6 i	petrol	LPG (Vialle)				
4. Volvo 850 GLT	petrol	LPG (Vialle)				
5. VW Transporter 2.0 i	petrol	LPG (Necam)		CNG (Necam)		
COMPRESSION IGNITION ENGINES						
6. Mercedes 250 D Turbo	diesel					
7. Nissan Sunny 2.0 D	diesel					
8. Peugeot 405 1.9 D	diesel					
9. VW Vento 1.9 TD	diesel					
10. Ford Transit 2.5 DI Turbo	diesel					

FEATURES						
	nr. cils	nr. valves/cils	fuel <sup>1)</sup> inj	3-way cat	EGR <sup>2)</sup>	other
1	4	4	mpi	+	-	variable valve timing variable intake system
2	4	4	mpi	+	-	
3	4	2	spi	+	+	
4	5	4	mpi	+	-	
5	4	2	spi	+	-	
	nr. cils	fuel <sup>3)</sup> inj.	turbo charg.	EGR <sup>2)</sup>	oxi cat	other
6	5	IDI electr.	+	+	+	autom. transm.
7	4	IDI	-	+	-	
8	4	IDI	-	-	-	
9	4	IDI	+	-	+	
10	4	DI	+	+	-	

- <sup>1)</sup> spi = single point injection  
mpi = multipoint injection  
<sup>2)</sup> EGR = Exhaust gas recirculation  
<sup>3)</sup> DI = Direct injection  
IDI = Indirect injection

Table 2.2: Driving patterns used

1	Coldstart European driving cycle	EDC	coldstart	2x
2	Warm European driving cycle	EDW	hotstart	1x
3	US '75 driving cycle	US	cold/hot	1x
4	Actual urban driving pattern	City	coldstart	2x
5	Actual traffic jam pattern	Jam	hotstart	1x

Table 2.3: Exhaust components analysed

Regulated components	CO total-HC NO <sub>x</sub> particulates
Additional components	CO <sub>2</sub> NO <sub>2</sub> (as NO <sub>x</sub> -NO)
Unregulated components	Aldehydes PAH C <sub>1</sub> - C <sub>5</sub> hydrocarbons C <sub>6</sub> - C <sub>12</sub> hydrocarbons nitro-PAH (limited)

Table 2.4: The aldehydes analysed

1	formaldehyde
2	acetaldehyde
3	acrolein
4	acetone
5	propionaldehyde
6	crotonaldehyde
7	methacrolein
8	n-butyraldehyde
9	benzaldehyde
10	i-valeraldehyde
11	n-valeraldehyde
12	o-tolualdehyde
13	m-tolualdehyde
14	p-tolualdehyde
15	hexanal

Table 2.5: The PAH analysed

1	fenanthrene
2	anthracene
3	fluoranthene
4	pyrene
5	3,6-dimethylfenanthrene
6	trifenylenes
7	benzo(b)fluorene
8	benzo(a)anthracene
9	chrysene
10	benzo(e)pyrene
11	benzo(j)fluoranthene
12	perylene
13	benzo(b)fluoranthene
14	benzo(k)fluoranthene
15	benzo(a)pyrene
16	dibenzo(a,j)anthracene
17	dibenzo(a,l)pyrene
18	benzo(g,h,i)perylene
19	dibenzo(a,h)anthracene
20	indeno(1,2,3-cd)pyrene
21	3-methylcholanthrene
22	anthanthrene

Table 2.6: C<sub>1</sub>-C<sub>5</sub> hydrocarbons analysed

1	methane
2	ethane
3	ethene
4	propane
5	propene
6	acetylene
7	i-butane
8	n-butane
9	i-butene
10	trans-butene
11	cis-butene-2
12	i-pentane
13	n-pentane

Table 2.7: C<sub>6</sub>-C<sub>12</sub> hydrocarbons analysed

1	benzene
2	cyclohexane
3	2-methylhexane
4	3-methylhexane
5	2,2,4-trimethylpentane
6	heptane
7	methyl-cyclohexane
8	toluene
9	2-methylheptane
10	3-methylheptane
11	n-octane
12	ethylbenzene
13	p,m-xylene
14	styrene
15	o-xylene
16	n-nonane
17	i-propylbenzene
18	n-propylbenzene
19	p,m-ethyltoluene
20	1,3,5-trimethylbenzene
21	o-ethyltoluene
22	1,2,4-trimethylbenzene
23	n-decane
24	1,2,3-trimethylbenzene
25	undecane
26	dodecane
27	naftalene

Table 2.8: Nitro-PAH analysed

1	2-nitro-fluorene
2	9-nitro-antrancene
3	3-nitro-fluorantene
4	1-nitro-pyrene
5	6-nitro-chrysene
6	7-nitro-benzo(a)antracene

### 3 SAMPLING AND ANALYSIS

Regulated exhaust gas components are measured according to strict procedures (for example 91/441/EEC). Since there is no legislation for unregulated components, prescribed and validated procedures are not (yet) available for the unregulated components. Also the interest in these components is relative new. Therefore the laboratories that perform these measurements, make use of the methods from other fields of experience, for example stationary sources. These methods for sampling and analysis have proven their applicability and are now more or less accepted in Europe. Because the interest in unregulated components is growing, international working-groups are formed to discuss and standardise the sampling and analysis methods. For example TNO takes part in an international working-group about the analysis of diesel particulates (including the determination of PAH).

#### 3.1 Sampling

In Fig. 3.1 the usual sampling system of car exhaust gases is shown. The exhaust gases are diluted by a factor of 10-15 in a so-called CVS (Constant Volume Sampler). This is done to avoid condensation or reactions between exhaust gas components during sampling. The system maintains a constant volumetric flow (hence the name) and the ratio between exhaust gases and dilution air depends on the exhaust gas flow. The dilution air is filtered. A sample of the diluted exhaust gas is drawn into a sampling bag, fabricated of 'Tedlar'. Since both the sample flow and the diluted exhaust gas flow are constant, the sampling is proportional at every moment. After the test the concentrations of the regulated pollutants in the sampling bag are analysed. The flow through the CVS-system is known from the system characteristics (in particular the venturi dimensions). Multiplication of concentrations and flow results in mass emissions. The concentrations of the diluted exhaust gas are corrected for those in the dilution air, which is sampled at the same time. In the case of diesel vehicles there is a long tube (a so-called tunnel) positioned between the mixing chamber and the sampling point, so as to obtain a fully developed turbulent flow. Through a second sample probe diluted exhaust gas is drawn through a pair of filters. These filters are weighed before and after the sampling and their weight increase is indicative for the particulate concentration of the diluted exhaust gas. Again by multiplication with the flow through the tunnel the total particulate emission may be calculated. The second filter serves to detect, and if necessary: correct for, any breakthrough of the first filter.



In Fig. 3.2 the additions are shown, necessary for the sampling of unregulated components. The tunnel was used for all tests (i.e. including the non-diesel tests). The determination of the composition of  $\text{NO}_x$  (in  $\text{NO}$  and  $\text{NO}_2$ ) can be made from the standard 'Tedlar' bag for the regulated components. The determination of  $\text{CO}_2$  can likewise be made from this bag. In fact, although  $\text{CO}_2$  is not as yet a regulated component, it is routinely measured with  $\text{CO}$ ,  $\text{HC}$  and  $\text{NO}_x$ , since its concentration plays a role in the determination of the dilution rate of the vehicle's exhaust gas. The light hydrocarbons ( $\text{C}_1\text{-C}_5$ ) are sampled by drawing a sample from the 'Tedlar' bag and storing it in a special aluminium coated bag. This bag is subsequently moved to the chemical laboratory for analysis by GC (gas chromatography). The heavier hydrocarbons ( $\text{C}_6\text{-C}_{12}$ ) are specially sampled in a metal tube containing 'Tenax'. 'Tenax' is an adsorbens consisting of small extremely porous plastic globules. Like the aluminium coated bag, the Tenax-tube is subsequently moved to the chemical laboratory for analysis. The aldehydes are sampled drawing a sample over a heated sample line and bubbling it through an impinger filled with an acidified acetonitrile solution, containing 2,4-dinitrophenylhydrazine (DNPH) reagents. This solution absorbs the aldehydes because the DNPH-reagents reacts with them. A second impinger is used to detect any breakthrough of the first one. The impingers are packed in ice to stabilise the components formed. Their contents are analysed in the chemical laboratory. The polynuclear aromatic hydrocarbons (PAH) are sampled in a two-stage set-up. The particle-bound PAH are caught on the filter used to sample the particulate emission. After weighing, the filters are moved to the chemical laboratory for analysis. The gaseous PAH are sampled on an adsorbens, 'Amberlite XAD-2', packed in a tube. Since this adsorbens turned out to contain PAH-components itself, it was carefully "washed" before use, to remove as much of the contamination as possible. After the test the tube with adsorbens is moved to the chemical laboratory. The sampling and analysis is further detailed in the additional reports [1] and [2].

### 3.2 Analysis

The regulated components are analysed by on-line analysers. They operate by non-dispersive infrared (NDIR) for  $\text{CO}$  and  $\text{CO}_2$ , flame ionisation detection (FID) for hydrocarbons and chemiluminescence (CL) for  $\text{NO}_x$ . The CL-analyser has two operating modes, measuring  $\text{NO}$  or  $\text{NO} + \text{NO}_2$  ( $\text{NO}_x$ ). The concentration of  $\text{NO}_2$  can be obtained by subtracting the reading for  $\text{NO}$  from that for  $\text{NO}_x$ . Because this means the subtraction of two near equal numbers, the resulting figure for  $\text{NO}_2$  is not very accurate. There is, however, no possibility to measure  $\text{NO}_2$  directly.

The TNO Institute of Environmental Sciences (IMW-TNO) carried out the analyses of the non-regulated components.

The light hydrocarbons ( $C_1$ - $C_5$ ) are analysed by gas chromatography, with FID in two steps. First methane is analysed. The other components have concentrations which are often lower to much lower (especially with petrol and CNG for fuel). The components are therefore concentrated first and then analysed gas-chromatographically.

The heavier hydrocarbons ( $C_6$ - $C_{12}$ ) are desorbed from the Tenax adsorbents and caught in a cold trap. The cold trap is subsequently heated and its contents is injected into a gas-chromatograph and analysed using FID. The results have the dimension ng/sample. A relevant concentration is obtained by referring the mass to the original sample flow, which therefore must be measured.

The aldehydes, trapped in an acidified solution of DNPH in acetonitrile, are analysed by reversed phase high performance liquid chromatography (RP-HPLC) combined with a UV-detector (the formed hydrazones are sensitive to ultraviolet). The results have the dimension ng/sample. A relevant concentration is obtained by referring the mass to the original sample flow, which therefore must be measured and, in this case, corrected to standard ambient conditions.

The PAH-containing particulate filters and the adsorbents XAD-2 are extracted with toluene for 16 hours in the dark, by means of soxhlet extraction. The extract is evaporated to nearly dry and subsequently solved in methanol. Analysis then takes place by RP-HPLC with fluorescence detection. The results have the dimension ng/sample. A relevant concentration is obtained by referring the mass to the original sample flow, which therefore must be measured and corrected to standard ambient conditions. To detect nitro-PAH, a zinc-column is installed before the analytical column. The nitro-PAH are reduced to the corresponding  $NH_2$ -PAH, which can be detected by fluorescence detection. The sampling and analysis is further detailed in the additional reports [1] and [2].

### 3.3 Accuracy

The concentration of the relevant components are in many cases very low. This is partly because the vehicles selected for the programme are provided with modern low emission technology and partly because the raw exhaust is diluted with ambient air before they are sampled. In a series of preliminary experiments it appeared that many components did not or hardly rise above the

detection limits, or did not rise sufficiently above the concentration in the dilution air. To overcome this problem the following steps were taken:

- \* The sample flows have been increased as much as possible.
- \* The dilution rate has been reduced as much as possible.
- \* Measures were taken to minimise the background concentration in the dilution air.

These measures minimised the influence of the background concentrations and thereby lowered the detection limit, but also increased the accuracy of the resulting numbers.

For the components measured from the 'Tedlar' bag a blank is available, because the dilution air is sampled in a similar way; this is a standard procedure which is performed at every measurement. For the  $C_1$ - $C_5$  determination a sample is transferred from the standard 'Tedlar' bag to a second aluminium coated bag. Once a day a similar sample is taken from the bag with dilution air, providing a blank for the  $C_1$ - $C_5$  samples of that day. For the other sampling systems a special blank run is made once a day. The entry for the vehicle's exhaust gas is then closed off and the pump-venturi system is drawing only dilution air through the tunnel. This air is sampled in the normal way. The samples are analysed as usual, providing the background (blank) values that are applied to all the testruns of that day.

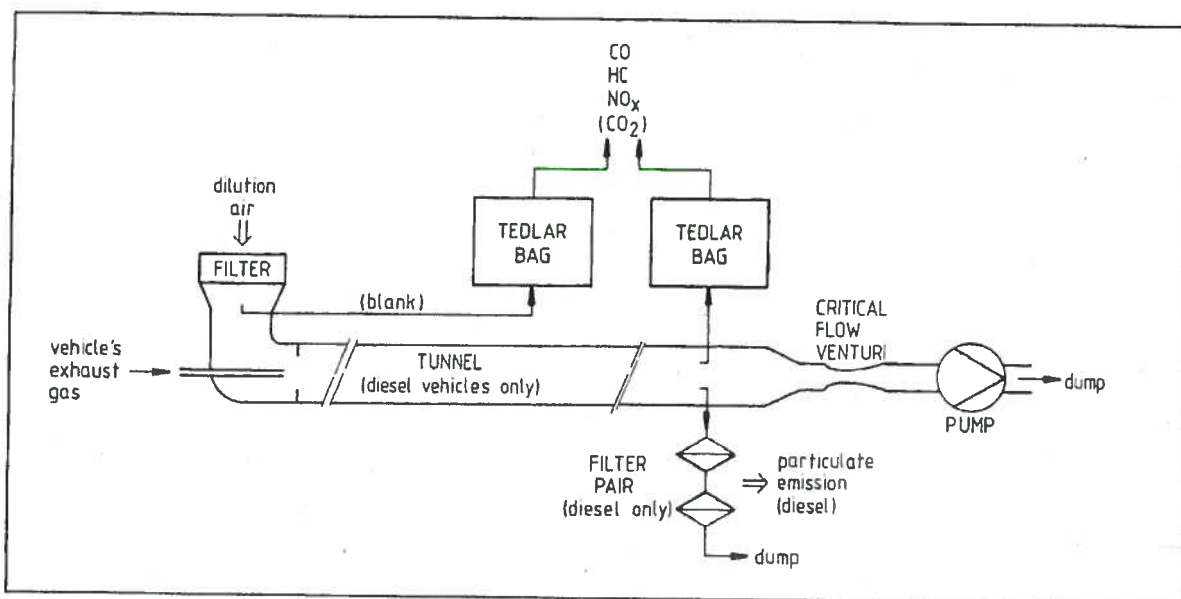


Figure 3.1: Conventional CVS sampling system (regulated components)

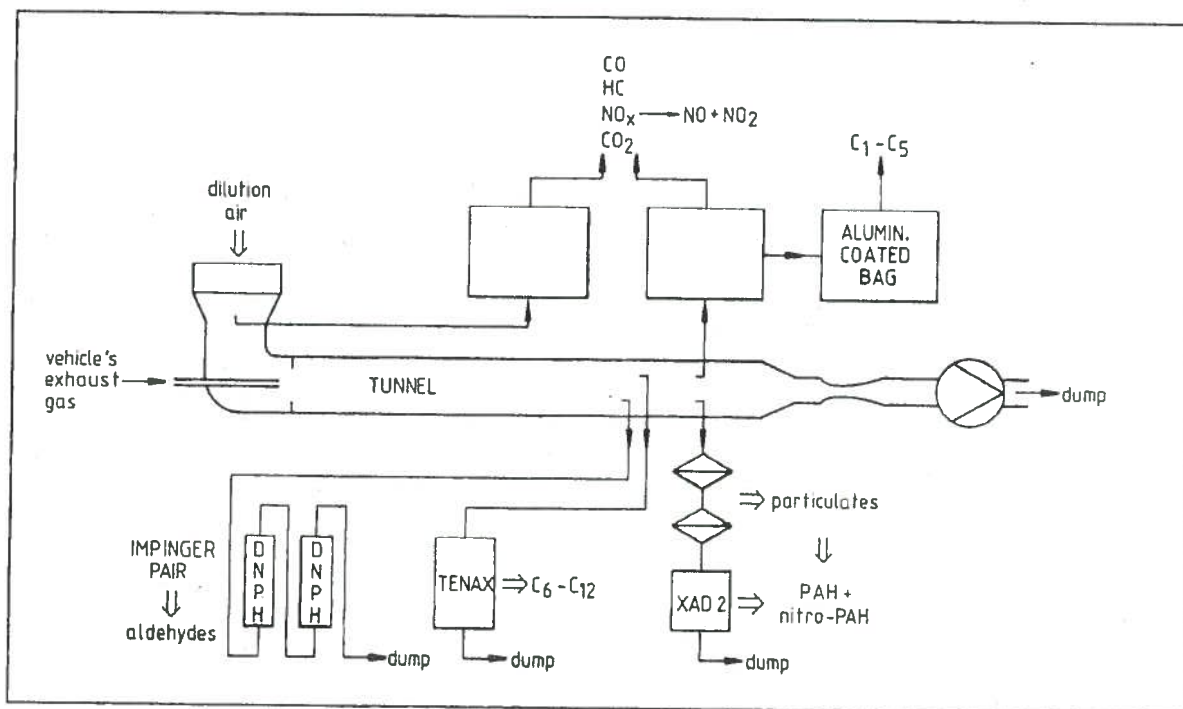


Figure 3.2: Adapted CVS sampling system (regulated and unregulated components)

#### 4 RESULTS

Detailed results are shown in [3]. For this present report in the first approximation the results have been averaged per fuel. The resulting emissions are shown in Tables 4.1 to 4.7 and Figures 4.1 to 4.7. Table 4.1 and Figure 4.1 show the results for the regulated components. The petrol vehicles show a relatively high CO-emission in all tests that start with a cold engine (and that in proportion to the relative weight of the cold part) and in the traffic jam. The same is true for the LPG, although the CO in the coldstart tests is less than for petrol. This can be explained by the fact that the increase in CO-emission in a coldstart test is partially caused by coldstart enrichment, which is less with gaseous fuels. In the warm European driving cycle the CO-emission is more or less the same for all fuels. The CO in the traffic jam is more on LPG than on petrol. The cause of this effect was traced to an insufficiently fine calibration of the LPG-control. In the meantime this has been rectified. The CNG-vehicles show a higher HC-emission than any other fuel. This is caused by a high emission of methane by the engine, which is not easily oxidised in the catalyst. The diesel engine is noteworthy for its relatively high emission of NO<sub>x</sub> and particulates. Especially in the traffic jam these emissions are high. Particulates are also high in the coldstart actual urban driving pattern

The emission of NO<sub>2</sub> as part of NO<sub>x</sub> (Table 4.2 and Fig. 4.2) amounts to about 11% for petrol and LPG and about 6% for CNG. For diesel it amounts to 25-30% of the total NO<sub>x</sub>. And since with diesel the total NO<sub>x</sub> is already high (4 to 5 times higher than with the other fuels), the amount of NO<sub>2</sub> exceeds that on other fuels by a factor of 10 (petrol and LPG) to 20 (CNG).

The emission of CO<sub>2</sub> is directly related to the fuel consumption. This in turn is very dependent on vehicle mass. Since the mass of the vehicles varies significantly, especially between small passenger cars and vans, the emission of CO<sub>2</sub> has also been calculated per 1000 kg of vehicle mass. In comparing these figures one should bear in mind, however, that an LPG-fuelled vehicle on average weighs 5% more than the petrol fuelled equivalent, and a diesel fuelled car between 5% and 7.5%. A CNG-fuelled car will lie somewhere between these figures.

The emission of CO<sub>2</sub> (Tables 4.3) and CO<sub>2</sub> per tonne (Fig. 4.3) is lowest with CNG, with the exception of the traffic jam situation. The CO<sub>2</sub>-emissions of LPG and Diesel are about equal for the European tests (coldstart and warm) and the actual urban driving pattern. Petrol scores highest on all cycles.

The traffic jam causes more than double the CO<sub>2</sub>-emissions of any other cycle (except for diesel).

The emission of C<sub>1</sub>-C<sub>5</sub> hydrocarbons is shown in Table 4.4 and Fig. 4.4. With petrol the main components apart from methane are the unsaturated ethene, propene and acetylene, plus n-butane, i-pentane and (to a lesser extent) n-pentane. Of these methane, ethene, i-pentane and for some cycles n-butane are the most important. With diesel fuel the main components are again the unsaturated ethene, propene and acetylene, with ethene as the most important. Methane is less important, but still noticeable. On LPG the main component is propane and then n-butane (the two main constituents of LPG) followed by methane and, to a much lesser extent, ethene, propene and i-butane. On CNG methane is by far the most important component (note the different scale in Fig. 4.3), followed at great distance by ethane. It is noteworthy that ~~methane plays an important role with all fuels except diesel. This has to do~~ with the fact that all spark ignition engines are fitted with catalysts and the conversion rate of methane in a catalyst is much lower than that for other components.

The emissions for C<sub>6</sub>-C<sub>12</sub> are shown in Table 4.5 and Fig. 4.5. The only fuel where concentrations of some significance are found is petrol. The main components of this group are benzene, toluene, xylene and 1,2,4 trimethylbenzene. With the other fuels the concentrations hardly rise above the detection level, with only in a relative sense some 'peaks' at benzene, and/or toluene, and/or xylene. So in all cases it is mainly or exclusively the BTX-group (benzene, toluene, xylene) that is of any importance.

The emissions of aldehydes are shown in Table 4.6 and Fig. 4.6. For all fuels formaldehyde is the most important component in this group. It is obvious, however, that for CNG the concentrations are an order of magnitude less than for petrol and LPG, while for diesel they are one to two orders of magnitude higher. Apart from formaldehyde the petrol vehicles emit also some acetaldehyde, acrolein, acetone and benzaldehyde. The LPG-fuelled vehicles emit, apart from formaldehyde, some acetaldehyde and in some cycles also some acrolein and acetone. The CNG-fuelled vehicles have no significant other aldehyde-emission apart from formaldehyde. Diesel vehicles, however, show a whole range of aldehyde-emissions in concentrations that decrease with increasing molecular size.

The emission of PAH is shown in Table 4.7 and Fig. 4.7. The main components are fenanthrene, fluoranthene and pyrene, three- and four-ring structures. The PAH-emissions of petrol, LPG and CNG are usually of the same order of magnitude, with the absolute values increasing in the order CNG, LPG and petrol. The PAH-emission of diesel engines is an order of magnitude higher



and there are also a number of other components that are emitted in noticeable quantities. The emissions in the traffic jam pattern and in the actual urban driving pattern are clearly higher than in the other cycles, and in the last mentioned condition also the petrol-fuelled vehicles emit other components (with five- and sixring structures).

The analysis of nitro-PAH at first showed no measureable results. The samples of all cycles driven were then combined for a number of vehicles. (Table 4.8) This provided measureable, though marginal results for two diesel vehicles. A third diesel vehicle showed a LC-peak that could be noticed, but was too weak to identify. In the samples of three other vehicles on petrol, LPG and CNG no nitro-PAH were found. This is in accordance with the low PAH-emissions of these fuels. Due to the fact that low levels were found in combined samples the evaluation of nitro-PAH was dropped from the results. The only conclusions that can be drawn is that diesel engines seem to have higher concentrations of nitro-PAH than engines on the other three fuels. This is to be expected, since both PAH and NO<sub>x</sub> are higher for diesel engines.

When comparing the different cycles one can draw the rough conclusion that the 'normal' driving conditions produce comparable results, with a certain increase in emissions in proportion to the weight of the coldstart on the whole cycle. The traffic jam pattern usually produces higher to much higher emissions than the 'normal' driving conditions, notwithstanding the fact that it is driven with a hot stabilised engine.

Table 4.1: Emission of regulated components (g/km)

City	Petrol	LPG	CNG	Diesel
CO	3.02	1.23	0.71	0.74
HC	0.47	0.18	0.61	0.16
NO <sub>x</sub>	0.28	0.36	0.14	0.77
Particulates	0.007	0.005	0.012	0.101

EDC				
CO	1.97	1.01	0.36	0.68
HC	0.27	0.15	0.37	0.12
NO <sub>x</sub>	0.18	0.15	0.17	0.78
Particulates	0.011	0.006	0.011	0.085

EDW				
CO	0.45	0.53	0.34	0.49
HC	0.10	0.09	0.17	0.09
NO <sub>x</sub>	0.13	0.10	0.14	0.74
Particulates	0.004	0.006	0.003	0.074

US	Petrol	LPG	CNG	Diesel
CO	1.12	0.91	0.45	0.67
HC	0.15	0.12	0.36	0.14
NO <sub>x</sub>	0.15	0.21	0.13	0.74
Particulates	0.015	0.005	0.025	0.094

Jam				
CO	4.50	7.44	0.19	1.96
HC	0.40	1.09	1.35	0.30
NO <sub>x</sub>	0.32	0.42	0.26	1.59
Particulates	0.008	0.010	0.006	0.157

Table 4.2: Emission of NO and NO<sub>2</sub> (g/km)

City	Petrol	LPG	CNG	Diesel
NO	0.15	0.19	0.09	0.36
NO <sub>2</sub>	0.05	0.06	0.01	0.22

EDC				
NO	0.11	0.09	0.11	0.38
NO <sub>2</sub>	0.02	0.02	0.01	0.20

EDW				
NO	0.08	0.06	0.09	0.37
NO <sub>2</sub>	0.01	0.01	0.01	0.17

US				
NO	0.09	0.13	0.09	0.35
NO <sub>2</sub>	0.01	0.02	0.01	0.21

Jam				
NO	0.19	0.26	0.17	0.73
NO <sub>2</sub>	0.03	0.03	0.01	0.49

Table 4.3: Emission of CO<sub>2</sub>/1000 kg vehicle mass (g/km)

City	Petrol	LPG	CNG	Diesel
CO <sub>2</sub> /1000 kg	175	155	143	158

EDC				
CO <sub>2</sub> /1000 kg	156	138	129	142

EDW				
CO <sub>2</sub> /1000 kg	144	127	122	130

US	Petrol	LPG	CNG	Diesel
CO <sub>2</sub> /1000 kg	163	144	136	141

Jam	Petrol	LPG	CNG	Diesel
CO <sub>2</sub> /1000 kg	390	334	322	284

Table 4.4: Emission of light hydrocarbons (C<sub>1</sub>-C<sub>5</sub>) (mg/km)

City	Petrol	LPG	CNG	Diesel
Methane	35	25	561	4.9
Ethane	4.3	2.8	21	0.46
Ethene	21	9.0	2.6	19
Propane	0.29	71	3.1	0.09
Propene	12	10	0.68	6.3
Acetylene	13	3.8	1.7	4.3
i-Butane	3.0	11	1.1	0.08
n-Butane	11	23	2.6	0.07
iso-Butene	3.3	1.1	0.56	1.6
trans-Butene	2.8	0.47	0.21	0.64
cis-Butene-2	1.1	0.22	0.11	0.13
i-Pentane	24	2.0	3.2	1.0
n-Pentane	7.2	0.64	1.3	0.06

EDC	Petrol	LPG	CNG	Diesel
Methane	23	22	385	3.9
Ethane	4.4	2.7	13	0.41
Ethene	16	8.4	1.6	18
Propane	1.2	50	1.4	0.22
Propene	9.1	8.7	0.17	6.0
Acetylene	6.9	2.2	0.27	4.5
i-Butane	1.9	7.5	0.19	0.09
n-Butane	6.7	16	0.35	0.12
iso-Butene	2.4	0.99	0.00	1.7
trans-Butene	2.9	0.63	0.00	0.79
cis-Butene-2	0.74	0.23	0.00	0.07
i-Pentane	12.5	0.60	0.19	0.84
n-Pentane	3.2	0.10	0.08	0.15

EDW	Petrol	LPG	CNG	Diesel
Methane	16	21	281	2.6
Ethane	2.6	2.5	6.9	0.30
Ethene	5.9	2.9	0.32	12
Propane	0.20	35	0.46	0.21
Propene	3.2	1.8	0.07	4.0
Acetylene	2.0	0.02	0.03	3.1
i-Butane	0.89	4.5	0.12	0.23
n-Butane	2.9	9.9	0.27	0.26
iso-Butene	0.85	0.21	0.00	1.1
trans-Butene	0.87	0.14	0.00	0.44
cis-Butene-2	0.19	0.04	0.00	0.05
i-Pentane	5.1	0.60	0.23	0.47
n-Pentane	1.3	0.18	0.10	0.16

US	Petrol	LPG	CNG	Diesel
Methane	24	23	398	3.2
Ethane	2.9	2.6	13	0.26
Ethene	9.5	7.3	1.1	12
Propane	1.1	55	0.80	0.11
Propene	5.5	6.8	0.11	3.8
Acetylene	5.3	2.0	0.49	2.3
i-Butane	2.4	6.3	0.32	0.02
n-Butane	8.3	19	0.72	0.13
iso-Butene	1.7	0.91	0.00	1.0
trans-Butene	2.2	0.68	0.00	0.30
cis-Butene-2	0.57	0.24	0.00	0.02
i-Pentane	15	1.8	1.0	0.24
n-Pentane	4.1	0.52	0.00	0.00

Jam	Petrol	LPG	CNG	Diesel
Methane	82	102	1530	8.6
Ethane	11	19	41	0.87
Ethene	18	43	0.27	32
Propane	0.57	523	1.3	0.37
Propene	9.4	43	0.11	9.8
Acetylene	3.1	6.3	0.68	9.6
i-Butane	3.7	67	0.03	0.14
n-Butane	14	160	0.06	0.30
iso-Butene	3.0	6.0	0.00	2.3
trans-Butene	4.4	3.3	0.00	1.2
cis-Butene-2	0.79	2.2	0.00	0.00
i-Pentane	25	8.0	0.00	0.92
n-Pentane	7.6	3.2	0.00	0.00

Table 4.5: Emission of heavier hydrocarbons (C<sub>6</sub>-C<sub>12</sub>) (mg/km)

City	Petrol	LPG	CNG	Diesel
Benzene	14	1.1	1.3	2.2
Cyclohexane	0.01	0.12	0.13	2.6
2-Methyl-hexane	6.0	0.75	0.84	0.16
3-Methyl-hexane	4.7	0.57	0.64	0.24
2,2,4-Methylpentane	3.6	0.79	0.48	1.0
Heptane	3.7	0.43	0.53	0.20
Methyl-cyclohexane	0.21	0.06	0.09	0.15
Toluene	39	2.7	3.3	1.6
2-Methyl-heptane	2.7	0.23	0.18	0.11
3-Methyl-heptane	2.4	0.18	0.16	0.13
n-Octane	1.3	0.08	0.08	0.30
Ethylbenzene	10	0.48	0.48	0.37
p,m-Xylene	36	1.6	1.5	1.1
Styrene	3.8	0.04	0.09	0.46
o-Xylene	12	0.50	0.49	0.29
n-Nonane	0.46	0.01	0.01	0.65
i-Propylbenzene	0.86	0.03	0.04	0.06
n-Propylbenzene	2.1	0.08	0.08	0.20
p,m-Ethyltoluene	7.2	0.21	0.16	0.32
1,3,5-Methylbenzene	4.4	0.13	0.14	0.40
o-Ethyltoluene	4.6	0.11	0.12	0.42
1,2,4-Methylbenzene	17	0.44	0.46	0.76
n-Decane	0.08	0.00	0.00	1.4
1,2,3-Methylbenzene	3.1	0.08	0.08	0.35
Undecane	0.73	0.01	0.02	1.5
Naftalene	1.9	0.02	0.03	0.87
Dodecane	0.07	0.00	0.01	0.74

EDC	Petrol	LPG	CNG	Diesel
Benzene	7.2	0.36	0.33	2.2
Cyclohexane	0.00	0.04	0.03	0.17
2-Methyl-hexane	3.0	0.17	0.16	0.38
3-Methyl-hexane	2.3	0.14	0.13	0.17
2,2,4-Methylpentane	2.4	0.16	0.15	0.68
Heptane	1.9	0.13	0.17	0.16
Methyl-cyclohexane	0.21	0.02	0.05	0.11
Toluene	19	1.2	0.93	1.1
2-Methyl-heptane	1.3	0.06	0.13	0.12
3-Methyl-heptane	1.2	0.05	0.08	0.14
n-Octane	0.63	0.03	0.08	0.26
Ethylbenzene	5.5	0.24	0.19	0.34
p,m-Xylene	17	0.67	0.66	0.65
Styrene	2.0	0.03	0.04	0.40
o-Xylene	6.7	0.23	0.24	0.31
n-Nonane	0.24	0.00	0.00	0.54
i-Propylbenzene	0.44	0.02	0.02	0.06
n-Propylbenzene	1.2	0.05	0.04	0.17
p,m-Ethyltoluene	2.8	0.12	0.09	0.28
1,3,5-Methylbenzene	2.2	0.08	0.08	0.30
o-Ethyltoluene	2.4	0.07	0.07	0.35
1,2,4-Methylbenzene	8.5	0.26	0.26	0.59
n-Decane	0.08	0.00	0.00	1.0
1,2,3-Methylbenzene	1.6	0.05	0.05	0.28
Undecane	0.38	0.01	0.01	1.1
Naftalene	0.62	0.01	0.03	0.79
Dodecane	0.04	0.00	0.00	0.71

EDW	Petrol	LEO	CNG	Diesel
Benzene	4.1	0.47	0.10	1.8
Cyclohexane	0.02	0.03	0.02	0.15
2-Methyl-hexane	1.8	0.12	0.06	0.25
3-Methyl-hexane	1.4	0.09	0.05	0.12
2,2,4-Methylpentane	2.2	0.09	0.14	0.49
Heptane	0.94	0.09	0.04	0.17
Methyl-cyclohexane	0.13	0.01	0.05	0.07
Toluene	8.6	0.72	0.47	0.84
2-Methyl-heptane	0.69	0.05	0.02	0.12
3-Methyl-heptane	0.59	0.04	0.02	0.10
n-Octane	0.27	0.03	0.01	0.22
Ethylbenzene	2.1	0.17	0.04	0.28
p,m-Xylene	7.1	0.59	0.12	0.56
Styrene	0.75	0.01	0.00	0.33
o-Xylene	2.5	0.23	0.05	0.25
n-Nonane	0.09	0.01	0.00	0.52
i-Propylbenzene	0.16	0.01	0.00	0.05
n-Propylbenzene	0.40	0.04	0.01	0.15
p,m-Ethyltoluene	0.91	0.06	0.01	0.20
1,3,5-Methylbenzene	0.75	0.06	0.01	0.26
o-Ethyltoluene	0.83	0.06	0.01	0.30
1,2,4-Methylbenzene	3.0	0.20	0.03	0.48
n-Decane	0.02	0.00	0.00	0.92
1,2,3-Methylbenzene	0.53	0.04	0.00	0.21
Undecane	0.15	0.00	0.00	0.97
Naftalene	0.21	0.03	0.00	0.65
Dodecane	0.02	0.00	0.00	0.64

US				
Benzene	5.8	1.1	0.46	1.9
Cyclohexane	0.00	0.04	0.03	0.16
2-Methyl-hexane	2.3	0.49	0.32	0.34
3-Methyl-hexane	1.8	0.38	0.26	0.20
2,2,4-Methylpentane	1.2	0.27	0.17	0.60
Heptane	1.4	0.35	0.21	0.20
Methyl-cyclohexane	0.15	0.03	0.03	0.11
Toluene	16	2.2	1.4	0.82
2-Methyl-heptane	1.1	0.19	0.11	0.09
3-Methyl-heptane	0.96	0.16	0.09	0.11
n-Octane	0.57	0.08	0.04	0.19
Ethylbenzene	4.2	0.46	0.26	0.31
p,m-Xylene	14	1.5	0.89	0.52
Styrene	1.7	0.05	0.04	0.33
o-Xylene	4.8	0.48	0.29	0.24
n-Nonane	0.20	0.01	0.01	0.56
i-Propylbenzene	0.35	0.04	0.02	0.05
n-Propylbenzene	1.1	0.09	0.04	0.16
p,m-Ethyltoluene	3.0	0.17	0.09	0.30
1,3,5-Methylbenzene	2.0	0.12	0.08	0.39
o-Ethyltoluene	2.1	0.12	0.06	0.34
1,2,4-Methylbenzene	7.5	0.43	0.24	0.56
n-Decane	0.04	0.00	0.00	1.2
1,2,3-Methylbenzene	1.4	0.07	0.04	0.30
Undecane	0.29	0.02	0.00	1.3
Naftalene	0.71	0.06	0.03	0.91
Dodecane	0.04	0.00	0.01	0.80

Jam				
Benzene	19	3.8	0.02	6.5
Cyclohexane	0.00	0.16	0.02	0.84
2-Methyl-hexane	8.1	1.5	0.04	0.99
3-Methyl-hexane	6.0	1.1	0.03	0.57
2,2,4-Methylpentane	7.1	0.57	0.00	1.4
Heptane	4.9	1.6	0.00	0.73
Methyl-cyclohexane	0.46	0.14	0.01	0.30
Toluene	46	8.7	0.00	2.8
2-Methyl-heptane	3.4	0.82	0.01	0.43
3-Methyl-heptane	2.9	0.64	0.00	0.37
n-Octane	1.7	0.40	0.00	0.76
Ethylbenzene	7.7	2.1	0.00	0.80
p,m-Xylene	32	6.6	0.02	1.7
Styrene	2.1	0.15	0.00	1.0
o-Xylene	11	2.4	0.00	0.78
n-Nonane	0.63	0.06	0.03	1.7
i-Propylbenzene	0.61	0.14	0.00	0.13
n-Propylbenzene	1.4	0.31	0.00	0.47
p,m-Ethyltoluene	3.2	0.64	0.00	0.62
1,3,5-Methylbenzene	3.3	0.54	0.00	0.72
o-Ethyltoluene	3.0	0.51	0.02	1.0
1,2,4-Methylbenzene	11	1.5	0.01	1.3
n-Decane	0.24	0.00	0.04	3.0
1,2,3-Methylbenzene	1.9	0.29	0.00	0.63
Undecane	0.55	0.04	0.02	3.1
Naftalene	1.0	0.05	0.03	1.9
Dodecane	0.07	0.00	0.00	2.0



Table 4.6: Emission of aldehydes (mg/km)

City	Petrol	LPG	CNG	Diesel
Formaldehyde	2.1	1.3	0.79	16
Acetaldehyde	1.3	0.77	0.31	8.6
Acrolein	0.45	0.30	0.08	5.3
Acetone	0.65	0.50	0.18	2.7
Propionaldehyde	0.14	0.04	0.00	1.6
Crotonaldehyde	0.09	0.03	0.03	1.4
Methacrolein	0.14	0.04	0.02	1.0
n-Butyraldehyde	0.14	0.02	0.00	0.85
Benzaldehyde	0.82	0.03	0.15	0.60
i-Valeraldehyde	0.01	0.00	0.00	0.24
n-Valeraldehyde	0.00	0.00	0.00	0.56
o-Tolualdehyde	0.15	0.00	0.00	0.05
m-Tolualdehyde	0.31	0.00	0.00	0.13
p-Tolualdehyde	0.25	0.00	0.00	0.09
Hexanal	0.00	0.00	0.00	0.14

EDC				
Formaldehyde	2.5	2.3	0.78	20
Acetaldehyde	1.4	0.99	0.16	8.4
Acrolein	0.52	0.30	0.01	4.9
Acetone	0.67	0.29	0.07	2.7
Propionaldehyde	0.18	0.04	0.02	1.5
Crotonaldehyde	0.12	0.04	0.02	1.5
Methacrolein	0.17	0.05	0.00	0.76
n-Butyraldehyde	0.12	0.04	0.02	0.75
Benzaldehyde	0.95	0.01	0.05	0.75
i-Valeraldehyde	0.01	0.00	0.00	0.06
n-Valeraldehyde	0.01	0.00	0.00	0.48
o-Tolualdehyde	0.23	0.00	0.00	0.23
m-Tolualdehyde	0.43	0.00	0.00	0.67
p-Tolualdehyde	0.24	0.00	0.00	0.18
Hexanal	0.00	0.00	0.00	0.13

EDW				
Formaldehyde	1.3	0.24	0.06	13
Acetaldehyde	0.75	0.15	0.06	5.8
Acrolein	0.27	0.03	0.00	3.2
Acetone	0.73	0.07	0.09	1.9
Propionaldehyde	0.04	0.00	0.00	0.93
Crotonaldehyde	0.08	0.00	0.00	0.90
Methacrolein	0.13	0.00	0.00	0.56
n-Butyraldehyde	0.06	0.00	0.00	0.51
Benzaldehyde	0.51	0.00	0.00	0.53
i-Valeraldehyde	0.00	0.00	0.00	0.02
n-Valeraldehyde	0.00	0.00	0.00	0.28
o-Tolualdehyde	0.14	0.00	0.00	0.19
m-Tolualdehyde	0.25	0.00	0.00	0.54
p-Tolualdehyde	0.14	0.00	0.00	0.02
Hexanal	0.00	0.00	0.00	0.06

US				
Formaldehyde	1.2	1.2	0.32	19
Acetaldehyde	0.65	0.53	0.07	7.6
Acrolein	0.23	0.18	0.02	4.6
Acetone	0.48	0.32	0.10	2.4
Propionaldehyde	0.07	0.03	0.00	1.4
Crotonaldehyde	0.08	0.02	0.00	1.4
Methacrolein	0.07	0.03	0.00	0.87
n-Butyraldehyde	0.06	0.02	0.00	0.73
Benzaldehyde	0.45	0.03	0.03	0.67
i-Valeraldehyde	0.00	0.00	0.00	0.23
n-Valeraldehyde	0.00	0.00	0.00	0.35
o-Tolualdehyde	0.10	0.00	0.00	0.07
m-Tolualdehyde	0.19	0.00	0.00	0.49
p-Tolualdehyde	0.11	0.00	0.00	0.22
Hexanal	0.00	0.00	0.00	0.14



Jam	Petrol	LPG	CNG	Diesel
Formaldehyde	2.5	3.1	0.11	61
Acetaldehyde	2.2	2.6	0.05	22
Acrolein	0.73	0.64	0.00	13
Aceton	0.45	0.79	0.04	11
Propionaldehyde	0.00	0.11	0.00	3.9
Crotonaldehyde	0.08	0.08	0.03	4.0
Methacrolein	0.29	0.12	0.00	2.0
n-Butyraldehyde	0.09	0.05	0.10	2.1
Benzaldehyde	0.75	0.16	0.19	2.1
i-Valeraldehyde	0.00	0.00	0.00	0.14
n-Valeraldehyde	0.00	0.00	0.00	0.78
o-Tolualdehyde	0.23	0.00	0.00	0.32
m-Tolualdehyde	0.39	0.00	0.00	0.17
p-Tolualdehyde	0.20	0.00	0.25	1.4
Hexanal	0.00	0.00	0.00	0.49

Table 4.7: Emission of PAH ( $\mu\text{g}/\text{km}$ )

City	Petrol	LPG	CNG	Diesel
Fenanthrene	12	4.3	3.2	28
Anthracene	2.6	0.44	0.21	1.9
Fluoranthene	3.7	1.7	0.96	11
Pyrene	3.9	1.3	1.1	12
3,6-Dimethylfenanthrene	0.37	0.20	0.26	1.7
Trifenylen	0.10	0.14		4.6
Benzo(b)fluorene	1.2	0.50		6.9
Benzo(a)anthracene	2.4	0.02	0.02	2.0
Chrysene	2.5	0.03	0.00	2.2
Benzo(e)pyrene	0.07	0.00	0.00	2.3
Benzo(j)fluoranthene	0.16	0.00	0.00	0.38
Perylene	0.44	0.00	0.02	0.34
Benzo(b)fluoranthene	1.6	0.00	0.01	1.1
Benzo(k)fluoranthene	1.2	0.02	0.01	0.53
Benzo(a)pyrene	2.2	0.04	0.04	1.4
Dibenzo(aj)anthracene	0.28	0.00	0.00	0.05
Dibenzo(al)pyrene	0.00	0.00	0.00	0.06
Benzo(ghi)perylene	4.1	0.09	0.06	1.5
Dibenzo(ah)anthracene	1.3	0.16	0.00	0.35
Indeno(1,2,3-cd)pyrene	3.0	0.03	0.00	1.5
3-Methylcholanthrene	0.09	0.00	0.00	0.06
Antanthrene	0.76	0.02	0.01	0.18

ELC	Petrol	LPG	CNG	Diesel
Fenanthrene	3.7	2.7	2.0	25
Anthracene	0.59	0.27	0.16	1.2
Fluoranthene	1.2	1.1	0.68	7.6
Pyrene	1.1	0.71	0.66	7.2
3,6-Dimethylfenanthrene	0.09	0.13	0.06	1.4
Trifenylen	0.32	0.05	0.00	2.2
Benzo(b)fluorene	0.39	0.44	0.25	3.3
Benzo(a)anthracene	0.30	0.06	0.00	0.83
Chrysene	0.29	0.09	0.00	1.5
Benzo(e)pyrene	0.00	0.00	0.00	1.6
Benzo(j)fluoranthene	0.07	0.00	0.00	0.31
Perylene	0.04	0.00	0.00	0.19
Benzo(b)fluoranthene	0.15	0.00	0.02	0.65
Benzo(k)fluoranthene	0.06	0.02	0.00	0.22
Benzo(a)pyrene	0.09	0.03	0.00	0.57
Dibenzo(aj)anthracene	0.01	0.00	0.00	0.06
Dibenzo(al)pyrene	0.01	0.00	0.00	0.07
Benzo(ghi)perylene	0.18	0.01	0.00	1.5
Dibenzo(ah)anthracene	0.18	0.00	0.00	0.59
Indeno(1,2,3-cd)pyrene	0.12	0.00	0.00	0.73
3-Methylcholanthrene	0.00	0.00	0.00	0.02
Anthracene	0.02	0.00	0.00	0.35

EDW	Petrol	LPG	CNG	Diesel
Phenanthrene	2.2	2.4	2.0	25
Anthracene	0.22	0.25	0.11	1.4
Fluoranthene	0.69	0.68	0.67	7.3
Pyrene	0.56	0.60	0.56	6.8
3,6-Dimethylphenanthrene	0.06	0.07	0.02	1.2
Trifenylen	0.11	0.01	0.00	1.9
Benzo(b)fluorene	0.20	0.50	0.00	3.1
Benzo(a)anthracene	0.04	0.05	0.00	0.79
Chrysene	0.07	0.00	0.00	1.1
Benzo(e)pyrene	0.00	0.00	0.00	1.6
Benzo(j)fluoranthene	0.00	0.00	0.00	0.39
Perylene	0.00	0.00	0.00	0.15
Benzo(b)fluoranthene	0.03	0.01	0.03	0.58
Benzo(k)fluoranthene	0.01	0.02	0.01	0.21
Benzo(a)pyrene	0.01	0.03	0.00	0.58
Dibenzo(a,j)anthracene	0.00	0.00	0.00	0.08
Dibenzo(a,l)pyrene	0.00	0.00	0.00	0.07
Benzo(ghi)perylene	0.01	0.04	0.00	1.3
Dibenzo(ah)anthracene	0.00	0.00	0.00	0.46
Indeno(1,2,3-cd)pyrene	0.02	0.02	0.00	0.58
3-Methylcholanthrene	0.00	0.00	0.00	0.01
Anthranthrene	0.00	0.00	0.00	0.09

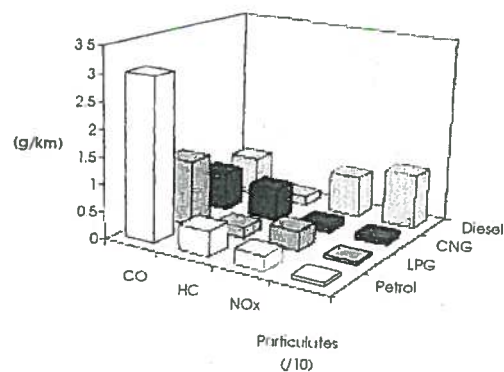
US				
Phenanthrene	4.6	3.4	2.3	35
Anthracene	0.89	0.34	0.29	2.1
Fluoranthene	0.95	0.73	0.74	11
Pyrene	1.0	0.71	0.65	13
3,6-Dimethylphenanthrene	0.11	0.10	0.09	20.0
Trifenylen	0.04	0.10		6.6
Benzo(b)fluorene	0.52	0.14	0.50	6.1
Benzo(a)anthracene	0.76	0.05	0.04	1.7
Chrysene	0.40	0.04	0.08	2.1
Benzo(e)pyrene	0.00	0.00	0.00	1.9
Benzo(j)fluoranthene	0.00	0.00	0.00	0.24
Perylene	0.08	0.00	0.01	0.33
Benzo(b)fluoranthene	0.25	0.00	0.03	1.2
Benzo(k)fluoranthene	0.20	0.02	0.01	0.45
Benzo(a)pyrene	0.34	0.04	0.11	1.1
Dibenzo(a,j)anthracene	0.04	0.02	0.08	0.11
Dibenzo(a,l)pyrene	0.00	0.01	0.03	0.04
Benzo(ghi)perylene	0.83	0.13	0.13	1.9
Dibenzo(ah)anthracene	0.24	0.25	0.91	0.15
Indeno(1,2,3-cd)pyrene	0.55	0.04	0.07	1.2
3-Methylcholanthrene	0.02	0.00	0.01	0.04
Anthranthrene	0.11	0.02	0.01	0.15

Jam				
Phenanthrene	9.3	7.4	6.6	54
Anthracene	2.0	0.50	0.61	2.2
Fluoranthene	1.9	2.1	2.1	17
Pyrene	2.2	1.5	1.9	18
3,6-Dimethylphenanthrene	0.17	0.29	0.00	2.8
Trifenylen	0.62	0.21		7.1
Benzo(b)fluorene	0.69	0.78	0.00	6.1
Benzo(a)anthracene	0.54	0.03	0.00	2.2
Chrysene	0.24	0.00	0.00	3.7
Benzo(e)pyrene	0.00	0.00	0.00	4.0
Benzo(j)fluoranthene	0.00	0.00	0.00	0.00
Perylene	0.39	0.00	0.00	0.47
Benzo(b)fluoranthene	0.01	0.00	0.00	1.6
Benzo(k)fluoranthene	0.00	0.00	0.00	0.64
Benzo(a)pyrene	0.02	0.00	0.00	1.8
Dibenzo(a,j)anthracene	0.12	0.00	0.00	0.15
Dibenzo(a,l)pyrene	0.00	0.00	0.00	0.13
Benzo(ghi)perylene	0.07	0.00	0.00	2.5
Dibenzo(ah)anthracene	0.00	0.00	0.00	0.70
Indeno(1,2,3-cd)pyrene	0.00	0.00	0.00	1.7
3-Methylcholanthrene	0.00	0.00	0.00	0.01
Anthranthrene	0.00	0.00	0.00	0.23

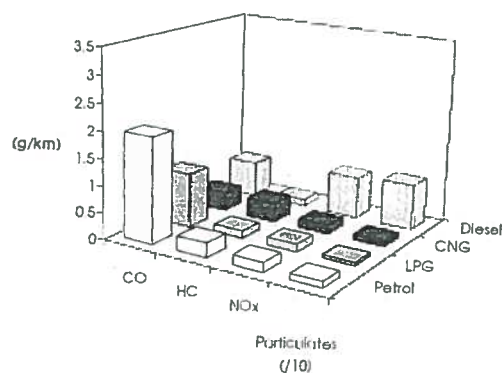
Table 4.8: Results from nitro-PAH determination

Peugeot 405	diesel	0.03 µg/km 1-nitropyrene
Mercedes 250 D	diesel	3 µg/km 1-nitropyrene 46 µg/km 2-nitrofluorene
Nissan Sunny	diesel	not quantifiable
Honda Civic	petrol	not detectable
Honda Civic	LPG	not detectable
Opel Vectra	CNG	not detectable

### Actual urban driving pattern



### Coldstart European driving cycle



### Warm European driving cycle

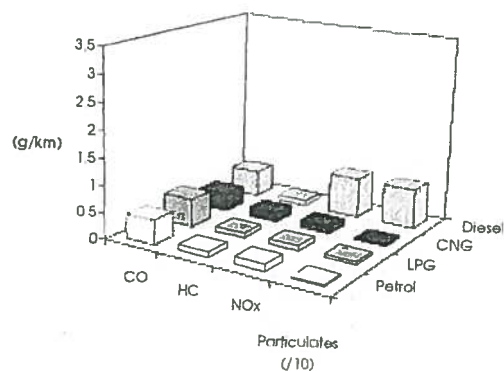


Figure 4.1a: Emission of regulated components

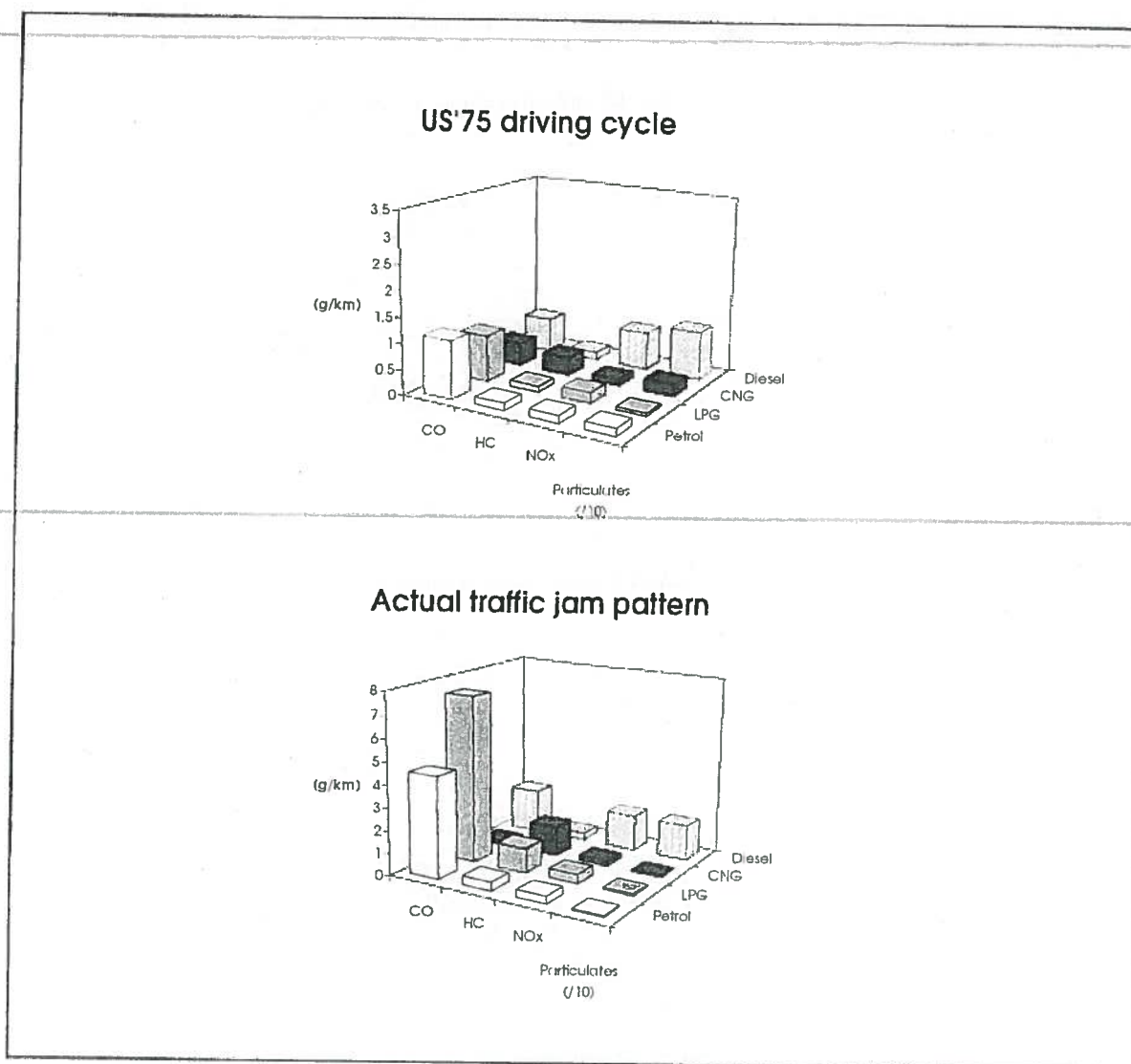
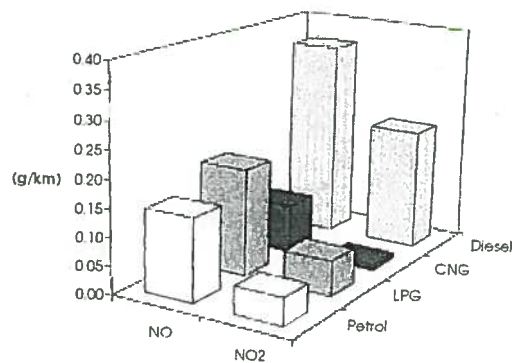
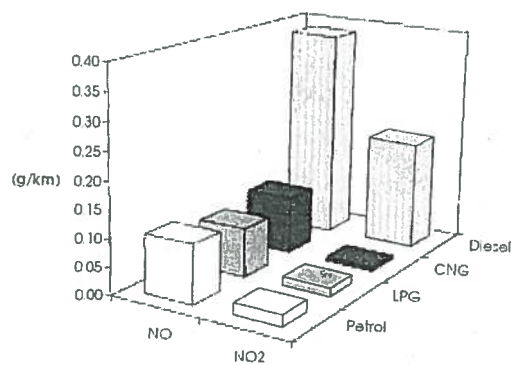


Figure 4.1b: Emission of regulated components (concluded)

### Actual urban driving pattern



### Coldstart European driving cycle



### Warm European driving cycle

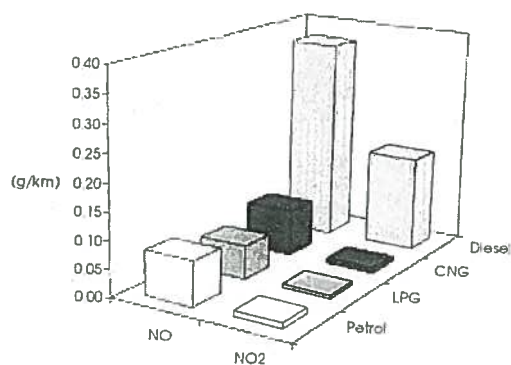
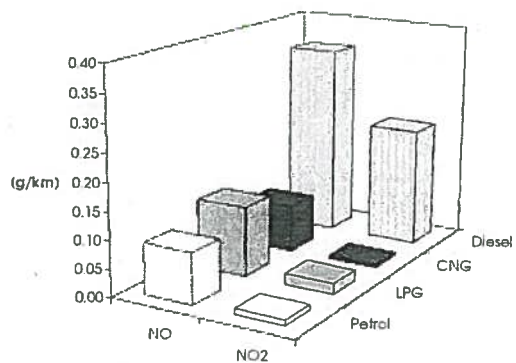


Figure 4.2a: Emission of NO and NO<sub>2</sub>

### US'75 driving cycle



### Actual traffic jam pattern

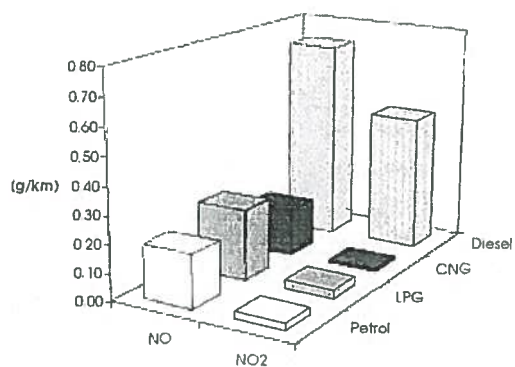


Figure 4.2b: Emission of NO and NO<sub>2</sub> (concluded)



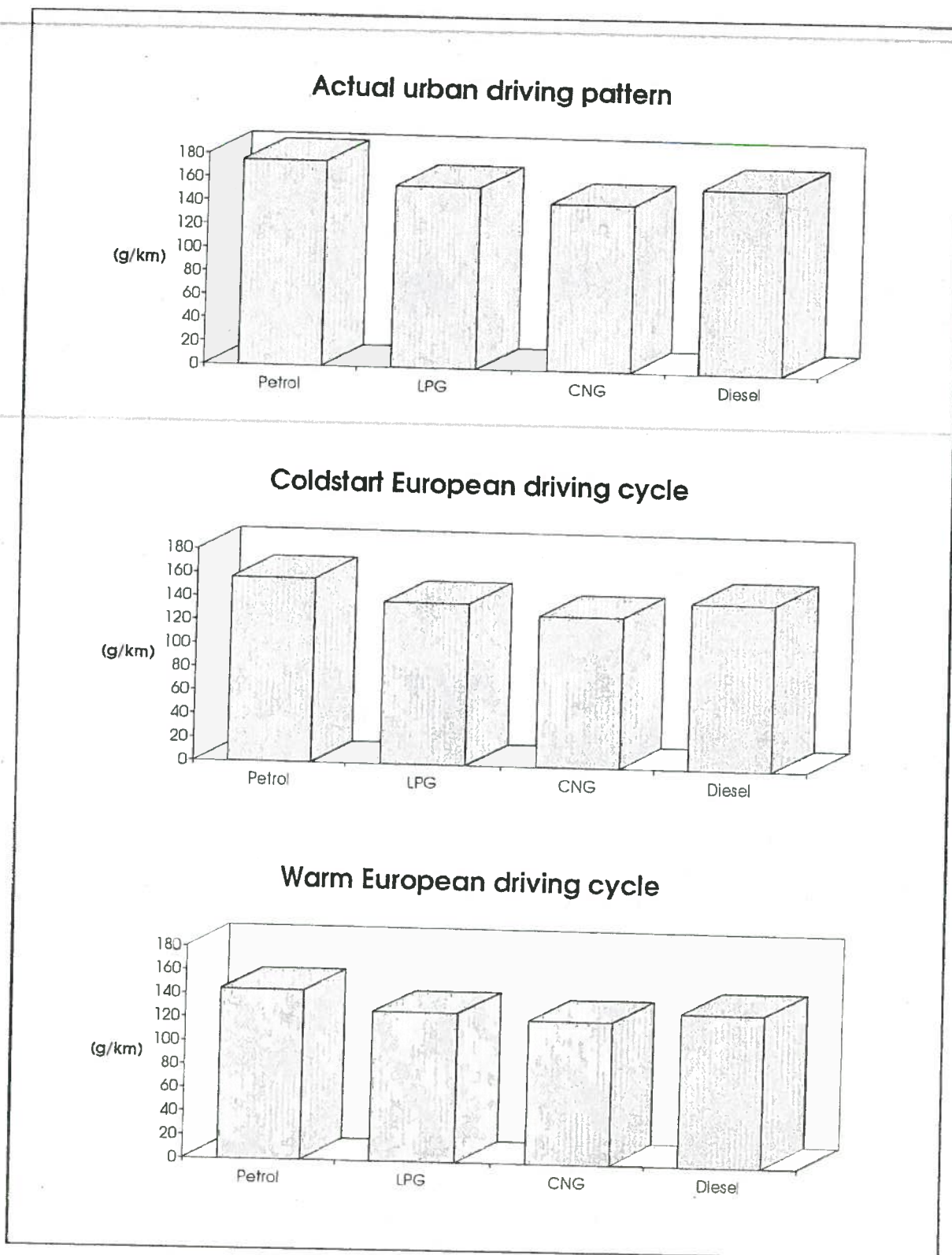


Figure 4.3a: Emission of CO<sub>2</sub>/1000 kg vehicle mass

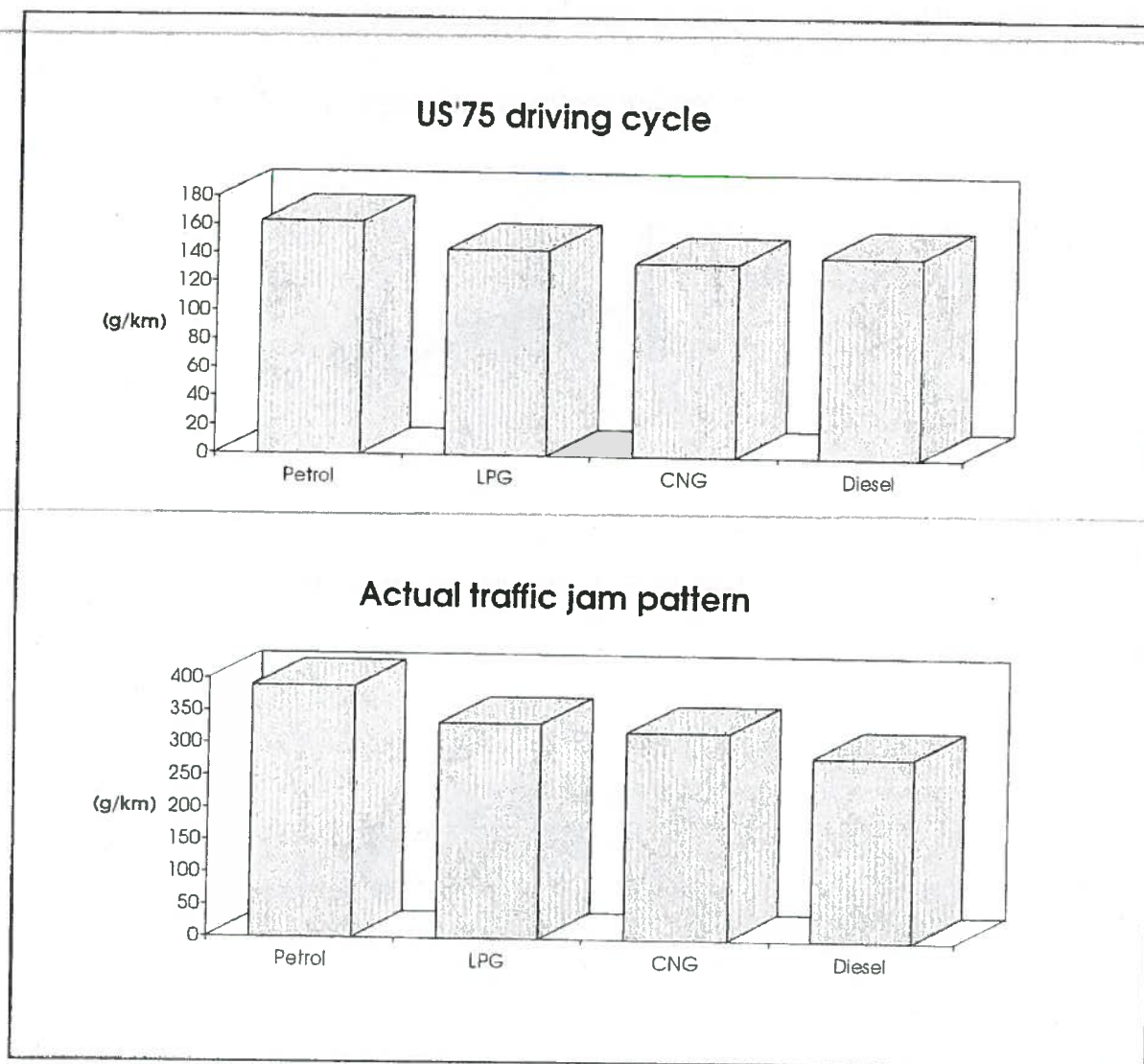
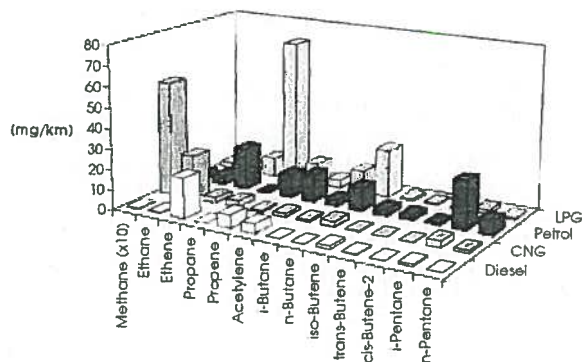
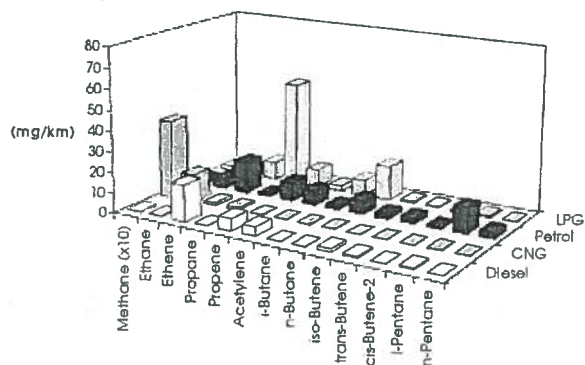


Figure 4.3b: Emission of CO<sub>2</sub>/1000 kg vehicle mass (concluded)

### Actual urban driving pattern



### Coldstart European driving cycle



### Warm European driving cycle

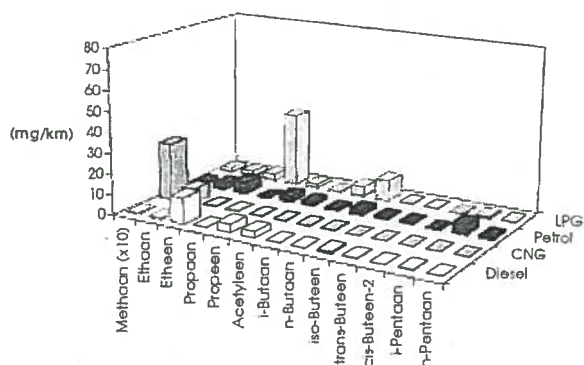


Figure 4.4a: Emission of light hydrocarbons (C<sub>1</sub>-C<sub>5</sub>)

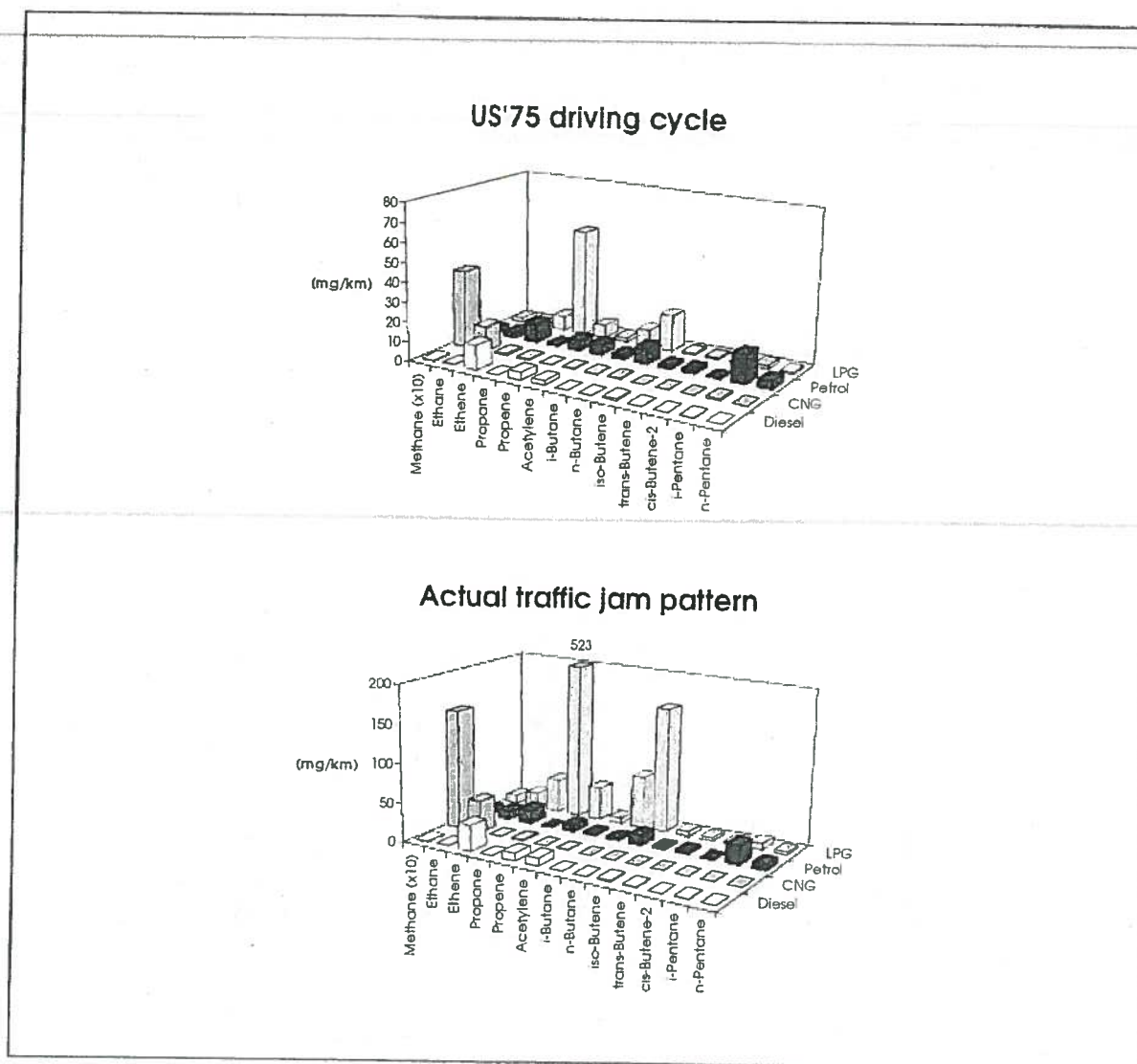


Figure 4.4b: Emission of light hydrocarbons ( $C_1-C_5$ ) (concluded)

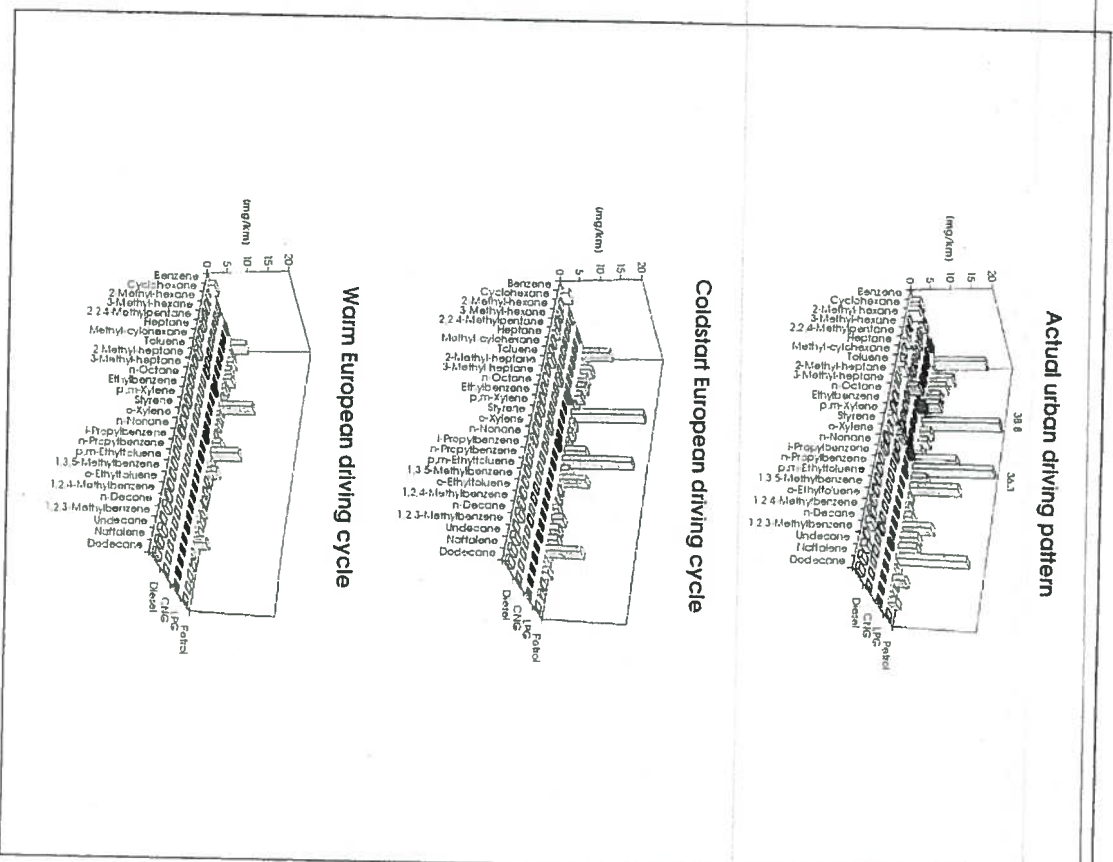


Figure 4.5a:

Emission of heavier hydrocarbons (C<sub>1</sub>-C<sub>12</sub>)

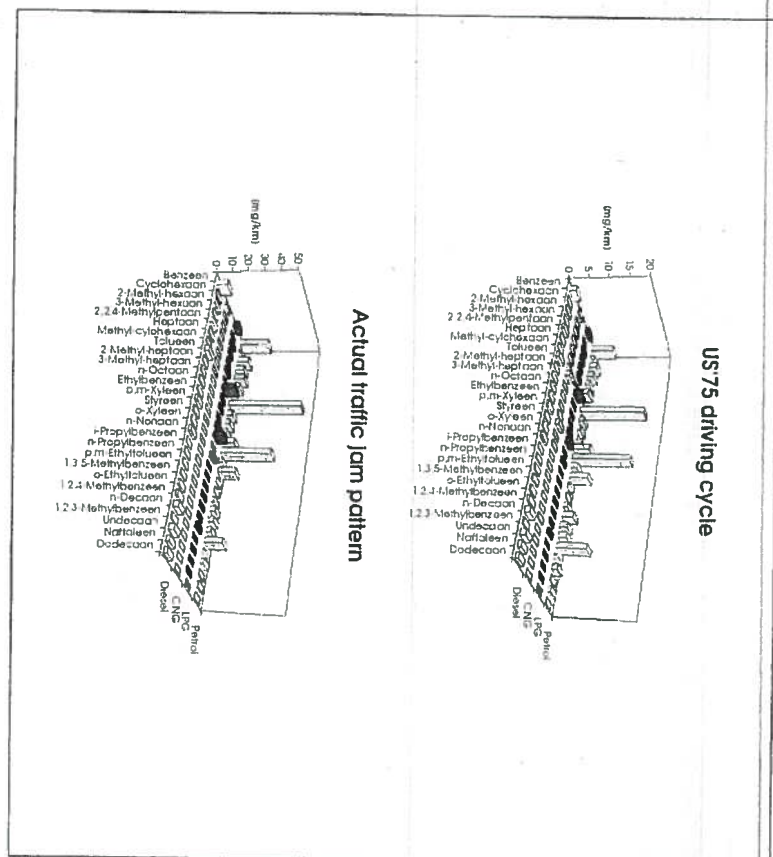


Figure 4.5b: Emission of heavier hydrocarbons ( $C_6-C_{12}$ ) (concluded)

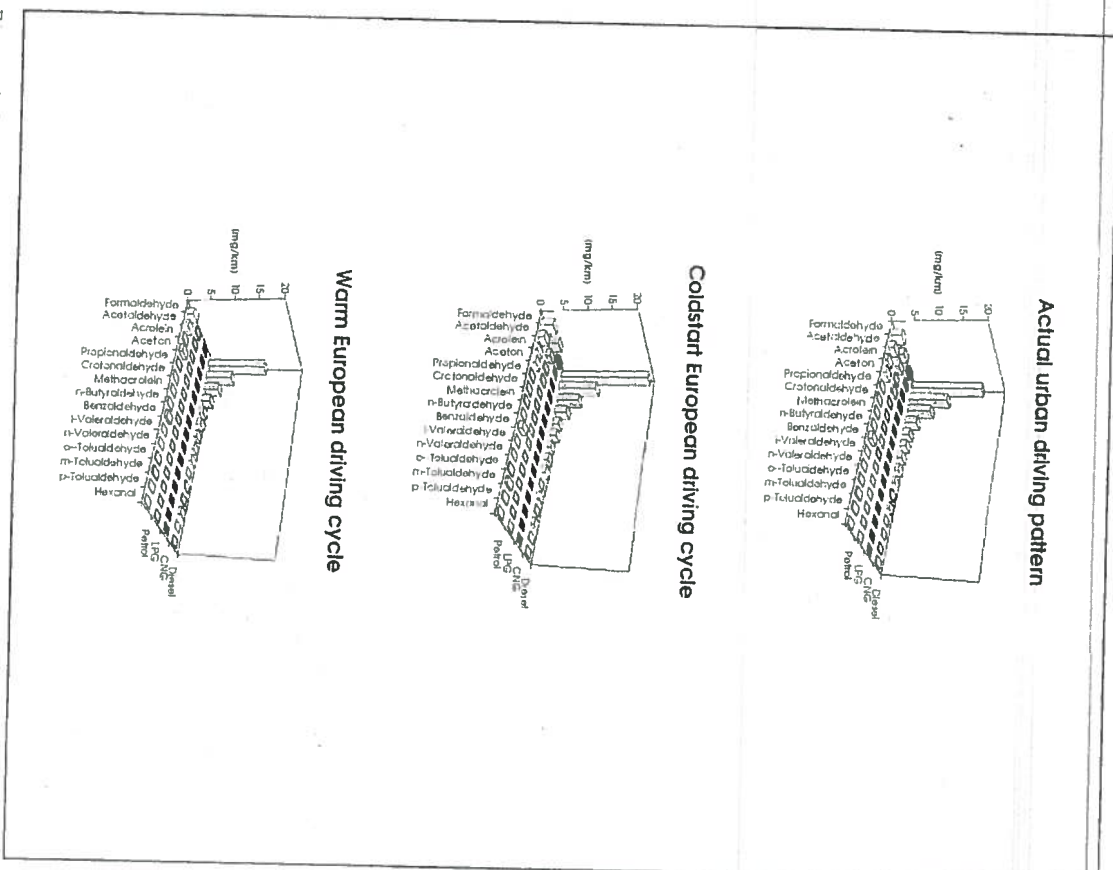


Figure 4.5a: Emission of aldehydes



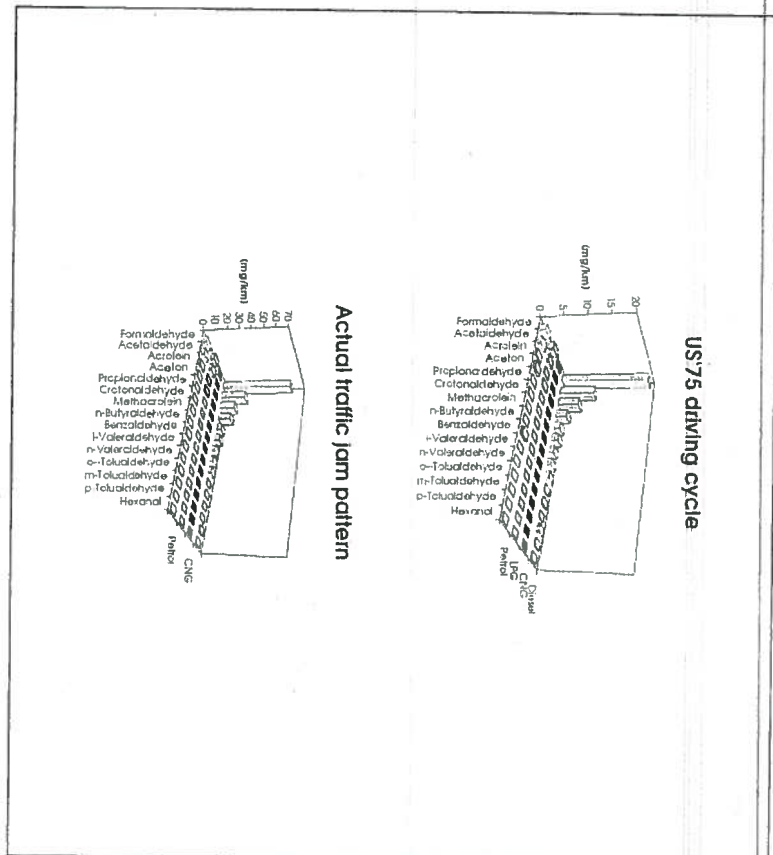
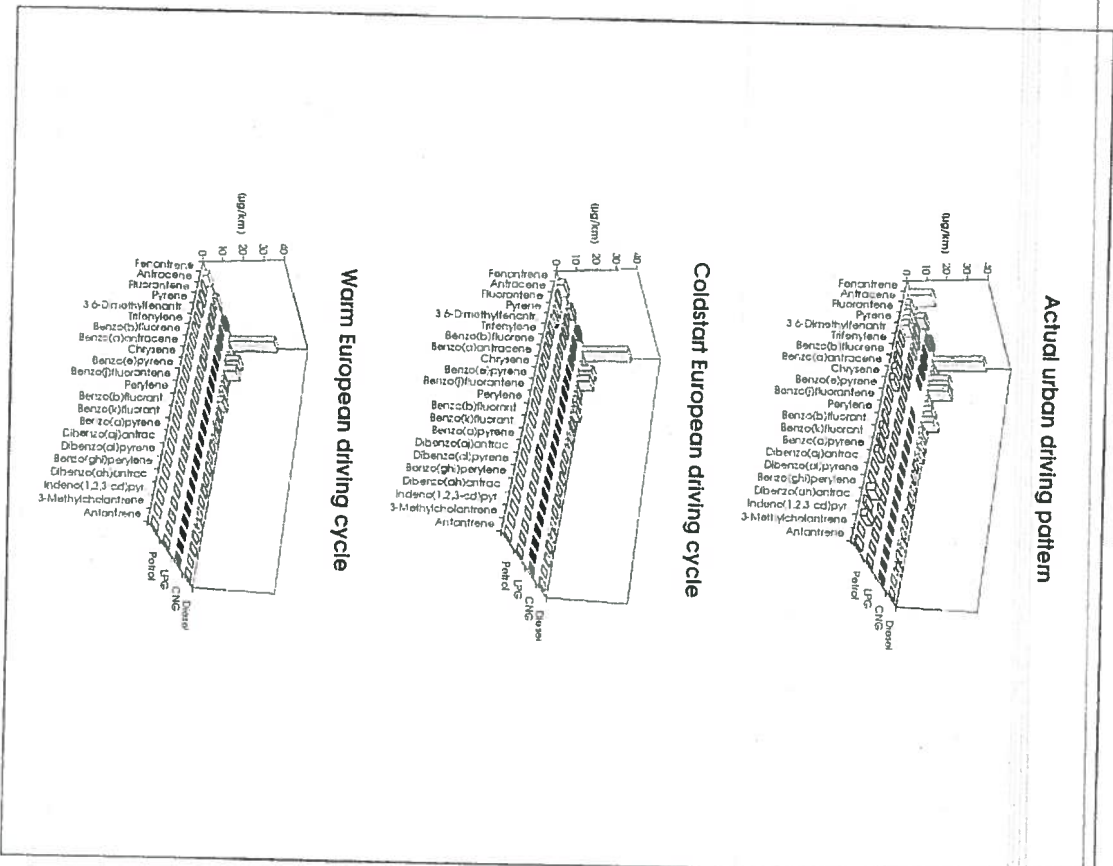


Figure 4. ob: Emission of aldehydes (concluded)



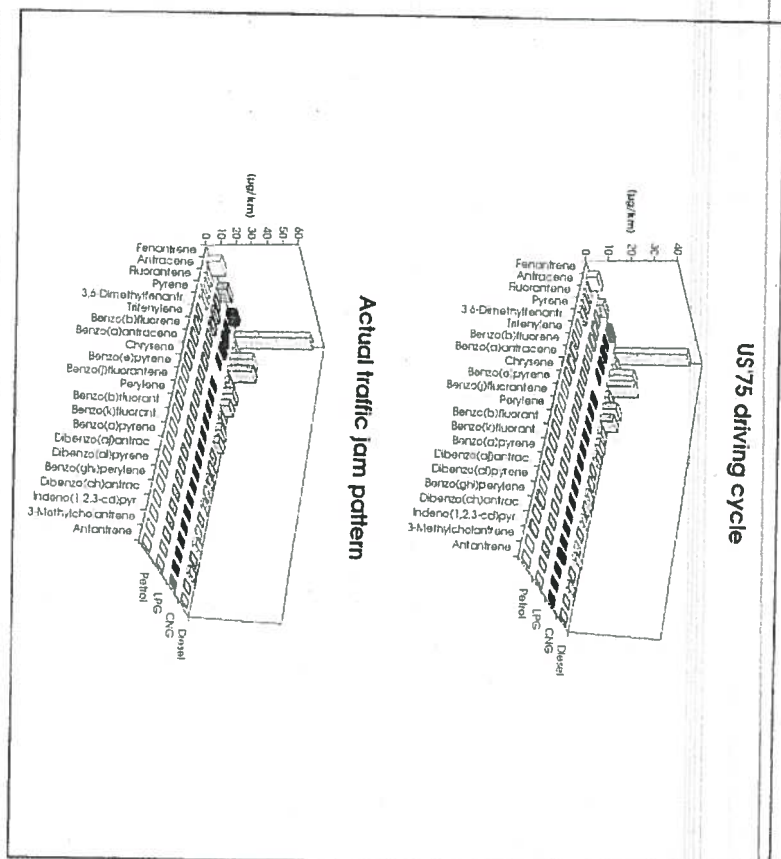


Figure 4.7b:

Emission of PAH (concluded)

## 5 ENVIRONMENTAL IMPACT

### 5.1 General considerations

Since the number of data from the programme, even if averaged per fuel, is large, an attempt was made to classify them according to environmental effects [5]. Such effects can be local, regional or global. Local could range from a street intersection to a city; regional could range from part of a country to a continent; global is everything that influences the whole planet. The local effects relate to toxic aspects or to direct nuisance caused by the exhaust gases. For practical reasons we have divided the toxic aspects into the direct toxic effects and long term toxic effects. Direct toxic and nuisance effects, are caused by CO, NO<sub>2</sub>, particulates and aldehydes these last mainly for local nuisance aspects; for this purpose only formaldehyde, acetaldehyde and acrolein are selected. Under the heading long term toxic effects the components are ranked that could cause cancer in the case of long term exposure. For this group the total emission of PAH, BTX (benzene, toluene, xylene) and the three lower aldehydes and ketones (formaldehyde, acetaldehyde and acrolein) have been selected. Regional effects considered are summersmog, wintersmog and acidification. Global effects include GWP (global warming potential) and ozone layer depletion. Since the impact of exhaust gases on the ozone layer may be regarded as insignificant, however, only GWP is considered in this study. So, to summarise, the following aspects are considered:

- \* Direct toxic and nuisance effects  
CO, NO<sub>2</sub>, particulates, formaldehyde +
- \* Long term toxic effects  
PAH, BTX, formaldehyde +
- \* Summersmog potential  
reactivity defined as ethene-equivalent: C<sub>1</sub>-C<sub>12</sub>, aldehydes, CO, NO<sub>x</sub>
- \* Wintersmog potential  
related to total particulate emission
- \* Acidifying potential  
acid equivalent expressed as mmol H<sup>+</sup>: NO<sub>x</sub> and SO<sub>2</sub>
- \* Global warming potential  
GWP expressed as CO<sub>2</sub>-equivalent: CO<sub>2</sub>, CO, CH<sub>4</sub>, NMHC, NO<sub>x</sub>

~~The direct toxic and nuisance effects have to be considered on a local scale~~  
and therefore per driving cycle. The long term toxic effects are dependent on  
~~the average use of a vehicle and have therefore been calculated over a~~  
weighted average of all cycles. Likewise the regional and global effects are  
dependent on the total use of a vehicle and have therefore been calculated  
over a weighted average of all cycles. When the weighting factors for the  
cycles were determined care was taken to get a mix of urban, extraurban,  
motorway and traffic jam kilometrage, as well as a coldstart/hot relationship  
that would approach the real world as closely as possible. This proved not  
completely possible: either the share in traffic conditions or the coldstart  
percentage would differ from the real. In the end two weightings were made:  
one for passenger car operation and one for light van operation (vans operate  
much more in urban areas than passenger cars). Care was taken to get the  
coldstart percentage right in both cases, as it was felt that this was an  
important factor, with the share in traffic conditions as a secondary  
requirement. As a consequence the share of urban traffic is overrepresented  
in the passenger car operation weighting and underrepresented in the light  
van operation weighting. The weighting factors are given below:

	pass.car	light van
Coldstart European Driving Cycle (EDC)	0.52	-
Warm European Driving cycle (EDW)	0.30	0.52
US'75 Driving cycle (US)	0.15	0.128
Actual Urban driving pattern (City)	0.027	0.35
Actual traffic jam pattern (Jam)	0.003	0.002

In order to characterise passenger car operation and light van operation it  
was decided not to limit this calculation to the 4 passenger cars and the 1  
van respectively, but to base the calculation on the average results of all 5  
vehicles in both cases. This seems to be acceptable since the results from  
the vans do not differ significantly from those of the passenger cars. And in  
mixing the results from the 5 vehicles a more representative average is  
obtained.

## 5.2 Direct toxic and nuisance effects

In Table 5.1 and Fig. 5.1 the selected components are shown for the 5  
different traffic situations for each of the four fuels. The emission of CO  
is generally highest with petrol and lowest with CNG and diesel. Peak values

~~are observed for the actual urban driving pattern and the traffic jam on petrol and again the traffic jam on LPG. The diesel too shows a marked increase in the traffic jam. By way of background information one should bear~~  
in mind that the CO-emission of petrol fuelled non-catalyst cars would have been around fivefold in the coldstart European driving cycle, and at least tenfold in the warm European driving cycle, the actual urban driving pattern and the traffic jam.

The emission of NO<sub>2</sub> is obviously highest for the diesel engine, especially in the traffic jam; in general it is an order of magnitude higher than for the other fuels. The NO<sub>2</sub> emissions on petrol and LPG have again a tendency to increase in the actual urban driving pattern and the traffic jam. The NO<sub>2</sub>-emission of non-catalyst petrol cars would have been in the order of the diesel figures.

The emission of particulates is again highest for the diesel vehicles, as would be expected. The diesel vehicles also peak again in the traffic jam. The petrol and CNG vehicles peak in the US'75 driving cycle.

The emission of formaldehyde + acetaldehyde + acrolein shows again values for the diesel engine that are an order of magnitude higher than for the other fuels, with again a peak in the actual traffic jam pattern. Of the other fuels the petrol and LPG do not differ very much, while CNG lies somewhat lower.

The merits or demerits of the various aspects can be qualified as shown in Table 5.4.a. A summary would show that petrol and LPG score about equal, with CNG better and diesel clearly worse. Of the non-diesel fuels only CO on petrol scores negative, but the emission of CO has improved already to such an extent that this may not be too relevant.

### 5.3 Longterm toxic effects

Longterm toxic effects are those effects that can become significant after long time exposure. In this study under this heading all those substances are considered that are suspected of carcinogenic properties. These are in the first place certain PAH-species, then some lower aromats like benzene, toluene and xylene (BTX) and finally some lower aldehydes and ketones (formaldehyde, acetaldehyde and acrolein). Ideally one should be able to give

~~all suspect components a 'score' and then add these scores together. This~~  
~~proved not possible. The actual causes of cancer are still ill-understood and~~  
~~we are far removed from a situation where we could give an exact score to~~  
individual compounds. Even, if some individual compounds can be ranked as  
carcinogenic, probably carcinogenic or possibly carcinogenic for humans, it  
is unknown how they would react in a cocktail of compounds. Known carcinogens  
can have their activity retarded by other components, while other compounds  
that are classified as not carcinogenic may act as stimulants for compounds  
that are carcinogenic. For this reason it was decided to group the components  
mentioned before into three groups, PAH, BTX and formaldehyde+, and to avoid  
the word carcinogenic.

Since the impact of longterm effects is related to overall exposure, the  
figures are summarised over the various cycles, according to the procedure  
and the weighting factors mentioned under 5.1. Table 5.2 and Fig. 5.2 list  
the relevant data. The first conclusion is that, with one exception, there is  
no real difference between the passenger car operation and the light van  
operation. The emission of PAH is clearly highest with the diesel vehicles.  
The gaseous fuels score slightly better than petrol. Remarkable is the  
relatively high score of petrol in the light van operation. This is due to  
the fact that in the light van mode the actual urban driving pattern is  
weighted relatively high and all five petrol vehicles show a high PAH-  
emission in this cycle (comp. Table 4.7 and Fig. 4.7). The emission of BTX is  
clearly highest for petrol, with little difference between the other fuels.  
In the case of formaldehyde+ it is again the diesel that scores highest,  
while the CNG scores lowest. The LPG scores slightly lower than petrol, but  
not in a significant way. A qualitative summary is made in Table 5.4.b:  
petrol and LPG score just below and just above average respectively, while  
CNG is clearly above average and diesel clearly below average. When the  
individual cycles are considered, there is little difference between urban  
and non-urban circumstances, apart from a coldstart effect on catalyst cars.  
A cycle that does lead to increased emissions, however, is the traffic jam:  
it consistently shows elevated emissions for almost all components.

#### 5.4 Regional and global effects

Although regional and global effects differ in scale, it seems best to take  
them together because both are concerned with total emissions rather than  
momentary (cycle dependent) emissions. It should be noted that only tailpipe



~~emissions are considered here. Evaporative emissions and so called indirect emissions (emissions due to production, transport, refining and distribution of fuels) are not part of this study (see for these aspects chapter 7).~~

Table 5.3 and Fig. 5.3 list the results from these effects. The first item considered is summersmog potential. Summersmog can be defined as the creation of photo-oxidants from  $\text{NO}_x$  and VOC (Volatile Organic Compounds) in the atmosphere. For the calculation the emissions of light and heavier hydrocarbons ( $\text{C}_1$ - $\text{C}_{12}$ ) and aldehydes have been used, as well as the emissions of  $\text{NO}_x$  and CO. Each organic compound is attributed a relative reactivity, defined as the mass of ozone formed per kg of compound, relative to the mass of ozone formed per kg of ethene. This approach is called the POCP-Concept (POCP = Photochemical Ozone Creation Potential). The POCP values of the various compounds are based on a typical European situation (which differs from e.g. a typical American situation). The resulting unit is grammes of ethene-equivalent. CO has a low POCP-value, but has a much greater mass, and therefore a significant influence. From Table 5.3.a it appears that the ethene-equivalent of LPG is average whereas that of diesel is more than twice as high, that of petrol is 50% higher and that of CNG is only a half.

Wintersmog is caused by  $\text{SO}_2$  and particulate matter. The contribution of light traffic to the total emission of  $\text{SO}_2$  is negligible, however, so the wintersmog potential is judged on the basis of the particulate emission. This is done in Table 5.3.b. This table shows that there is little real difference between the fuels, with the exception of diesel. This conclusion is in line of course with that on the local emission of particulates (see 5.2).

For the acidification  $\text{NO}_x$  and  $\text{SO}_2$  are considered. Two other components that can cause acidification are  $\text{NH}_3$  and  $\text{HCl}$ , but they play no part in traffic. For these components an acidifying effect may be calculated as  $\text{mmol H}^+$ . This allows summation of the various components (here  $\text{NO}_x$  and  $\text{SO}_2$ ). It is true that  $\text{SO}_2$  has not been measured, but the  $\text{SO}_2$ -emission can be easily calculated from the fuel consumption and the fuel sulfur content. The results are given in Table 5.3.b. It appears that the spark ignited versions do not differ very much (although there is a small advantage for the gaseous fuels), but that the diesel exhaust gas emits a factor 3-5 more acidifying products. This is particularly due to the higher emission of  $\text{NO}_x$ .

For the global warming potential  $\text{CO}_2$ , CO,  $\text{CH}_4$ , NMHC (non-methane hydrocarbons) and  $\text{NO}_x$  are considered. Some of these components have a direct greenhouse

Table 5.1: Direct toxic and nuisance effects

CO (g/km)	Petrol	LPG	CNG	Diesel
City	3.0	1.2	0.7	0.7
EDC	2.0	1.0	0.4	0.7
EDW	0.5	0.5	0.3	0.5
US	1.1	0.9	0.5	0.7
Jam	4.5	7.4	0.2	2.0

a

NO <sub>2</sub> (mg/km)				
City	50	60	10	220
EDC	20	20	10	200
EDW	10	10	10	170
US	10	20	10	210
Jam	30	30	10	490

b

Particulates (mg/km)				
City	7	5	12	101
EDC	11	6	11	85
EDW	4	6	3	74
US	15	5	25	94
Jam	8	10	6	157

c

Formaldehyde + Acetaldehyde + Acrolein (mg/km)				
City	3.9	2.4	1.2	30
EDC	4.4	3.6	0.9	33
EDW	2.3	0.4	0.1	22
US	3.9	2.4	0.4	32
Jam	5.4	6.3	0.2	96

d

Table 5.2: Long-term toxic effects

PAH ( $\mu\text{g}/\text{km}$ )	Petrol	LPG	CNG	Diesel
Pass. car operation	9	5.5	4.0	62
Light van operation	19	6.5	4.5	68

a

BTX ( $\text{mg}/\text{km}$ )				
Pass. car operation	42	3	2	4
Light van operation	53	4	3	4

b

Formaldehyde + Acetaldehyde + Acrolein: $\text{mg}/\text{km}$				
Pass. car operation	3.5	2.5	0.5	29
Light van operation	3.0	1.5	0.5	26

c

Table 5.3: Regional and global effects

Summersmog: ethene equivalent in $\text{mg}/\text{km}$	Petrol	LPG	CNG	Diesel
Pass. car operation	195	130	70	305
Light van operation	215	145	75	295

a

Wintersmog potential: total particulates in $\text{mg}/\text{km}$				
Pass. car operation	9	6	11	84
Light van operation	6	6	9	86

b

Acidification: $\text{mmol H}^+/\text{km}$				
Pass. car operation	5.0	3.0	3.5	18
Light van operation	5.5	4.5	3.0	17

c

GWP: $\text{CO}_2$ -equivalent in $\text{g}/\text{km}$				
Pass. car operation	240	210	200	235
Light van operation	245	215	205	240

d

Table 5.4: Evaluation of effects

Direct toxic and nuisance effects	Petrol	LPG	CNG	Diesel
CO	o	o/+	++	+
NO <sub>2</sub>	o	o	+	--
particulates	o/+	+	o	-/--
lower aldehydes	o	o	+ / ++	- / --

a

Long-term toxic effects				
PAH	o	+	+	-
BTX	-	o	o	o
lower aldehydes	o	o	+	-
summary	-/o	o/+	+	-

b

Regional and global effects				
summersmog	-	o	+	--
wintersmog	o	o/+	o	-
acidification	o	o/+	o/+	-
GWP	-/o	o	o/+	-/o
summary	-/o	o/+	o/+	-

c

Summary of effects				
Dir. Toxic	o	o/+	+ / ++	- / --
LT Toxic	-/o	o/+	+	-
Reg./global	-/o	o/+	o/+	-

d

++ much better than average

+ better than average

o average

- worse than average

-- much worse than average

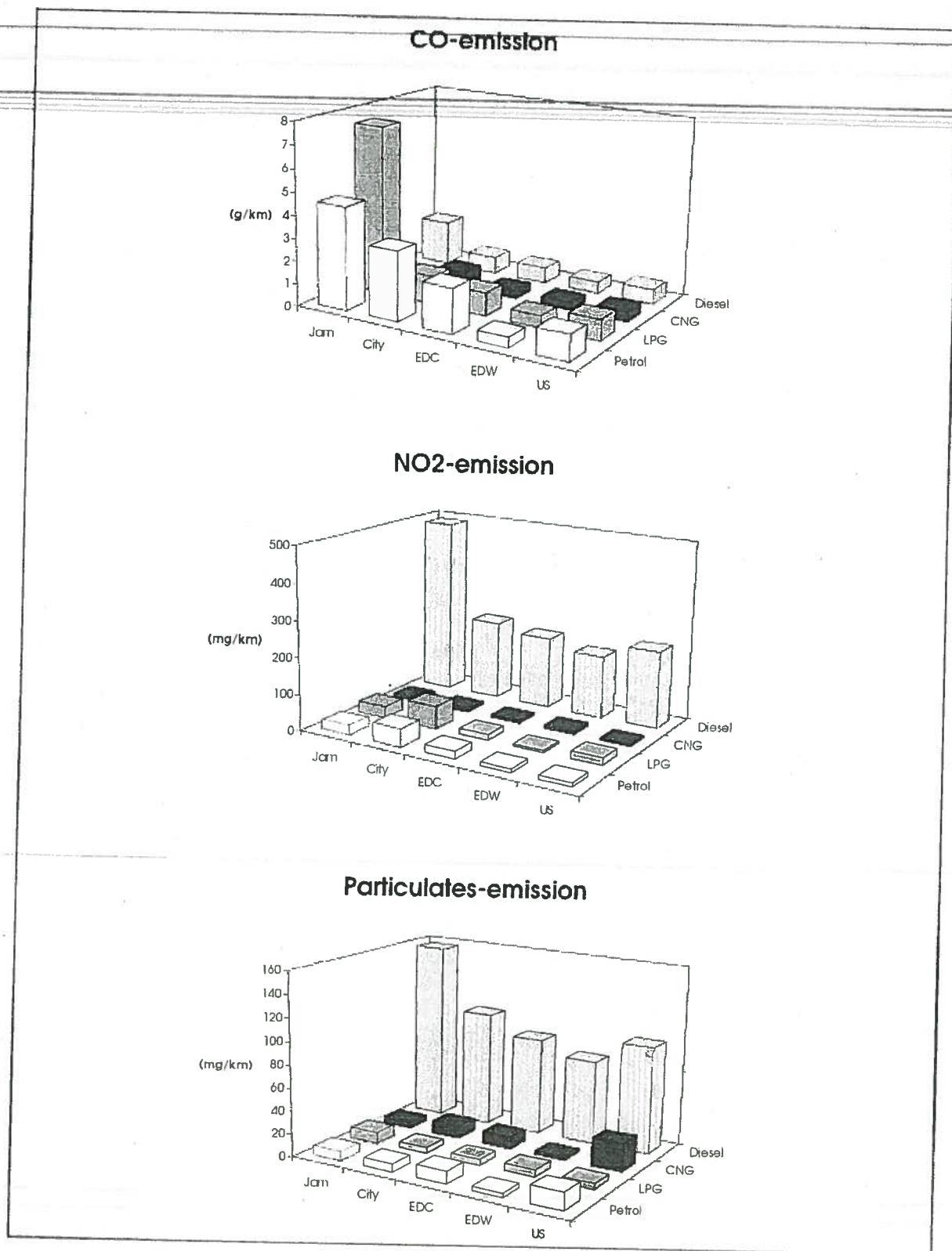


Figure 5.1a: Direct toxic and nuisance effects

### Formaldehyde + Acetaldehyde + Acrolein

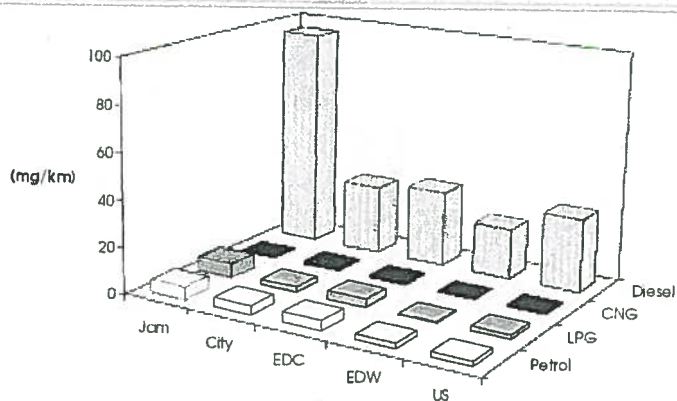


Figure 5.1b: Direct toxic and nuisance effects (concluded)



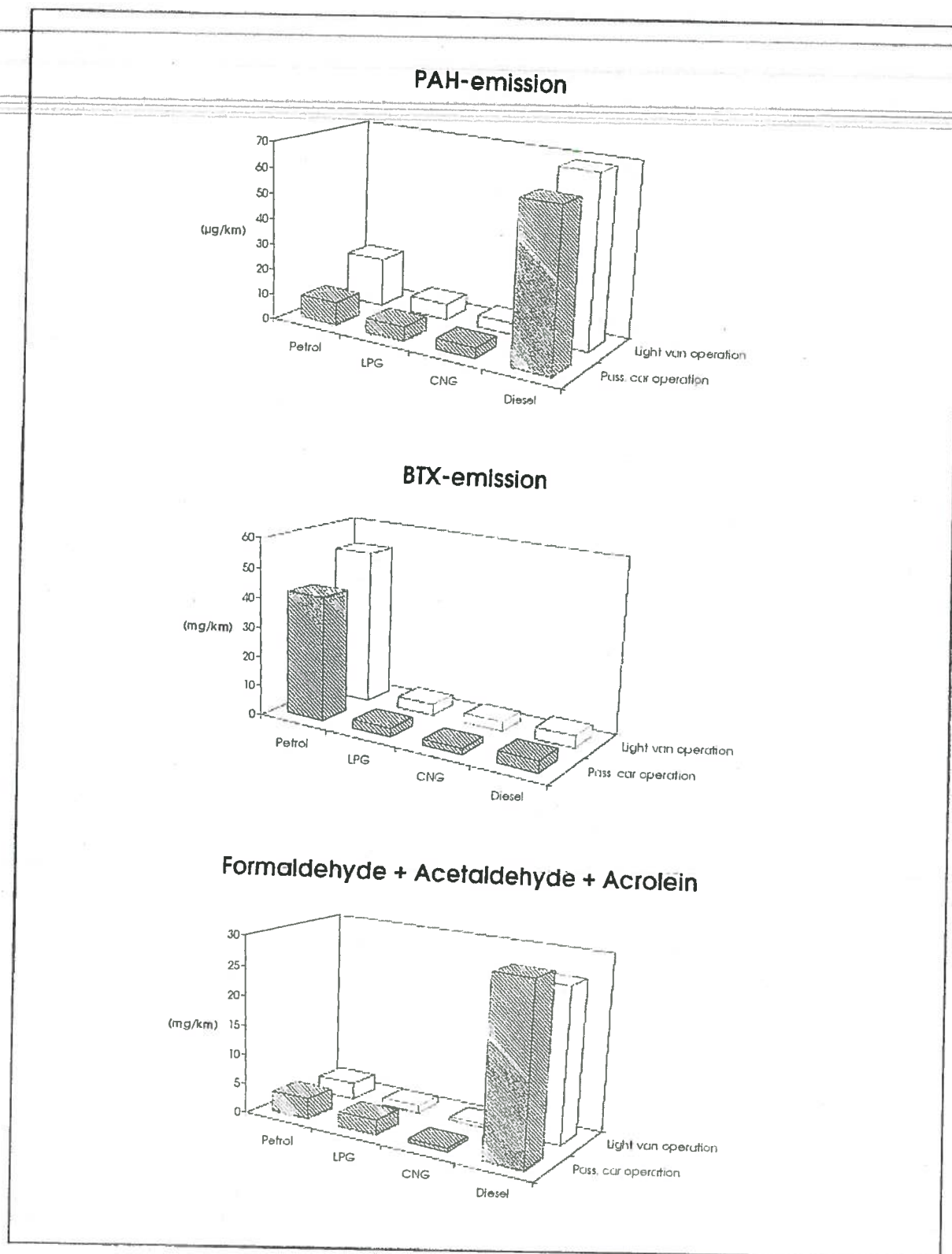
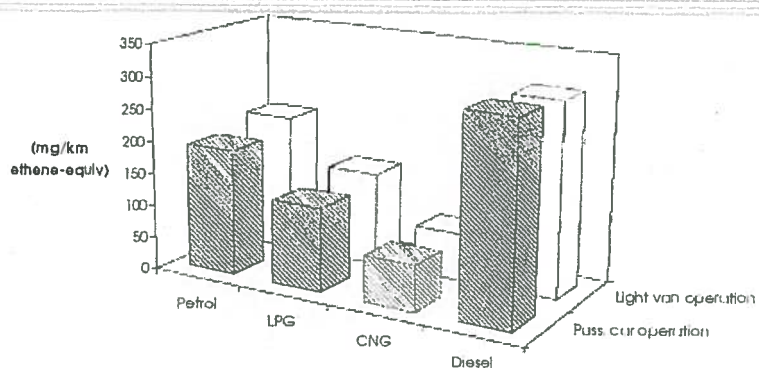


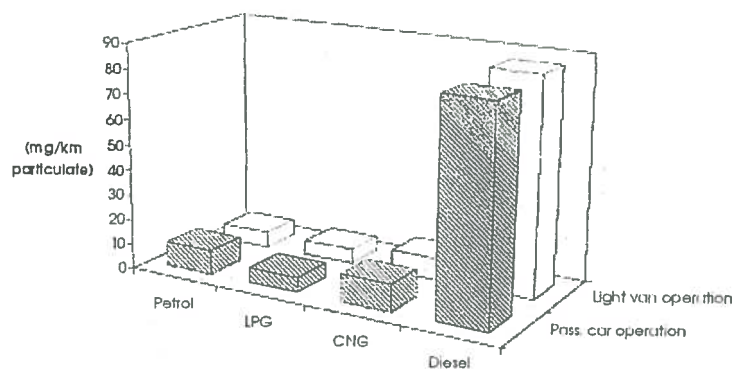
Figure 5.2: Long-term toxic effects



### Summersmog potential



### Wintersmog potential



### Acidification

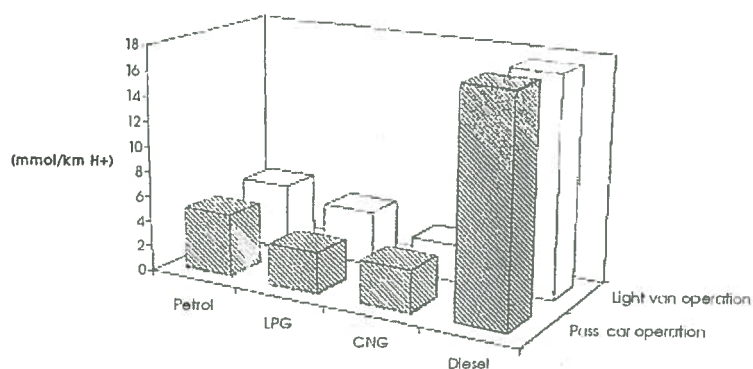


Figure 5.3a: Regional and global effects

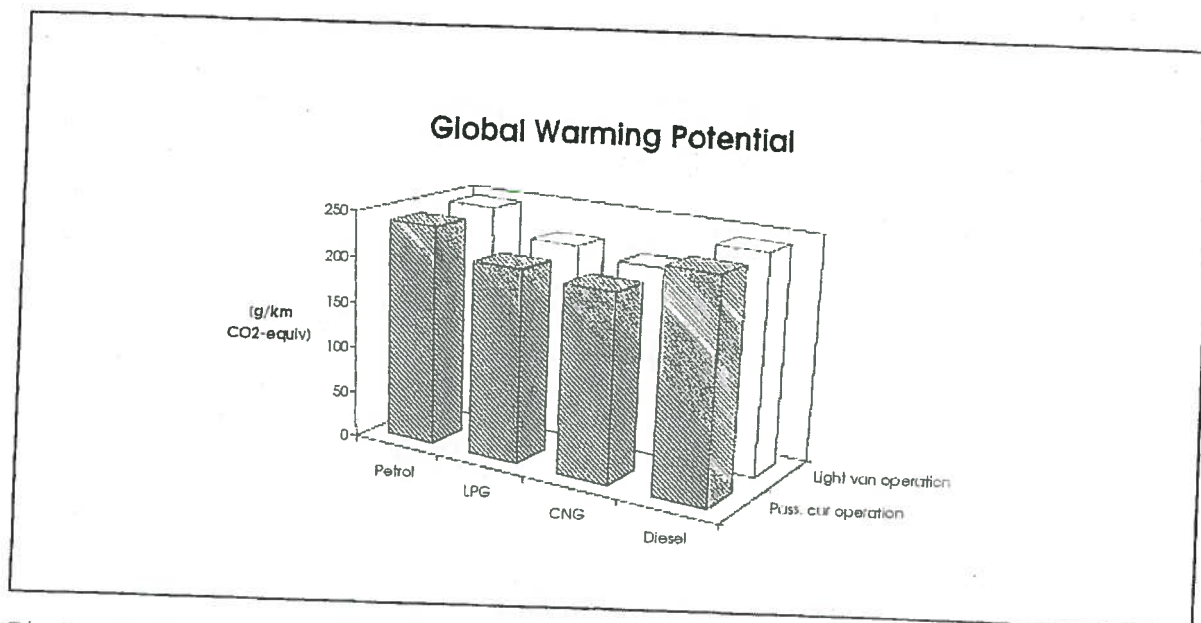


Figure 5.3b: Regional and global effects (concluded)

## 6 OTHER COMPARISONS

### 6.1 Coldstart effects

The bulk of measured data allows other comparisons to be drawn such as the impact of a cold started engine on the emissions. This impact is obviously different for spark ignition engines and compression ignition (diesel) engines. There might be differences between the three fuels for spark ignition operation as well. A large difference between coldstart emissions and hotstart emissions means that relatively more is emitted in urban surroundings, since the proportion of 'cold' kilometers in urban surroundings is higher than in non-urban areas. The only possibility to check this is to compare the coldstart European driving cycle (EDC) with the warm European driving cycle (EDW) since this is the same cycle in both cases. The US '75 driving cycle and the actual urban driving pattern also start from cold, but have not been measured with a hotstart. The European driving cycle is assumed to be fairly representative of average European use, however. On the other hand the ambient temperature of at least 20°C in the laboratory tends to underestimate the coldstart emissions.

In Table 6.1 and Figure 6.1 the coldstart and hotstart figures are shown for the directly toxic effects. For the petrol fuelled cars the coldstart effect is significant, although the absolute figures are low for all components except CO. Approximately the same is true for LPG. In the case of CNG there is only a large coldstart effect for the lower aldehydes and for particulates. In the case of particulates the accuracy of the absolute values is such, however, that no real conclusions can be drawn. The high value in the coldstart test is completely due to a high value scored by the light van in one of the cold cycles, but not in the repeat test (38 mg versus 3 mg). It is thought that this is caused by oil consumption on that particular engine. The highest values for most components (except CO) are scored by the diesel engines. But for these engines the coldstart effect is only small, with the possible exception of formaldehyde+.

In Table 6.2 and Figure 6.2 the relevant figures are shown for the long-term toxic effects. For petrol engines the coldstart emissions are about twice as high as the hotstart ones, which is especially important in the case of BTX, where the petrol engine scores highest anyway. For the LPG engines only the

emission of the lower aldehydes makes a large difference. The same is true for CNG, but in that case the emission of BTX also shows a significant effect, albeit at a low absolute level. Diesel also shows a difference for the lower aldehydes, not so big in a relative sense but quite high in an absolute sense. The other emissions are low or do not show a real difference between coldstart and hotstart.

In Table 6.3 and Figure 6.3 the regional and global effects are shown, although these are by definition not relevant on an urban scale. Only in cities as big as London could e.g. summersmog have an urban scale. In this table petrol and LPG stand out in relation to summersmog. The other fuels do not stand out or have a low absolute emission in urban surroundings. GWP is usually judged on a smaller scale as far as differences are concerned. In that case all fuels show a 7-12% decrease when the engine is warm. These differences are of the same order for all fuels.

So with regard to toxics the urban environment is charged with a more than average emission of CO with petrol and LPG, most of the emission of lower aldehydes on LPG and CNG (but at a low absolute level) and a more than average emission of BTX on petrol (and on CNG, but at a low absolute level). On diesel there is a mildly elevated level of lower aldehydes in an urban environment.

Of the regional and global effects the urban traffic makes a more than average contribution to summersmog in the case of petrol or LPG and a moderately increased contribution to acidification in the case of LPG.

Table 6.1: Coldstart effects on direct toxic components

CO (g/km)	Petrol	LPG	CNG	Diesel
coldstart	1.97 (100)	1.01 (100)	0.36 (100)	0.68 (100)
hotstart	0.45 ( 23)	0.53 ( 53)	0.34 ( 96)	0.49 ( 72)

NO <sub>2</sub> (mg/km)				
coldstart	21 (100)	16 (100)	8 (100)	199 (100)
hotstart	10 ( 48)	6 ( 38)	10 (133)	174 ( 87)

Formaldehyde+ (mg/km)				
coldstart	1.97 (100)	1.01 (100)	0.36 (100)	0.68 (100)
hotstart	0.45 ( 23)	0.53 ( 53)	0.34 ( 96)	0.49 ( 72)

Particulates (mg/km)				
coldstart	21 (100)	16 (100)	8 (100)	199 (100)
hotstart	10 ( 48)	6 ( 38)	10 (133)	174 ( 87)

Table 6.2: Coldstart effects on long-term toxic effects

PAH: µg/km	Petrol	LPG	CNG	Diesel
coldstart	8.9 ( 100)	5.6 (100)	3.8 (100)	57.0 (100)
hotstart	4.2 ( 47)	4.7 ( 83)	3.4 ( 89)	54.5 ( 96)

Formaldehyde+: mg/km				
coldstart	4.4 (100)	3.6 (100)	0.9 (100)	32.8 (100)
hotstart	2.3 ( 52)	0.4 ( 12)	0.1 ( 12)	21.7 ( 66)

BTX: mg/km				
coldstart	49.9 (100)	2.4 (100)	2.2 (100)	4.3 (100)
hotstart	22.4 ( 45)	2.0 ( 83)	0.7 ( 34)	3.4 ( 80)

Table 6.3: Coldstart effects on regional and global environmental effects

Wintersmog: mg part./km	Petrol	LPG	CNG	Diesel
coldstart	11 (100)	6 (100)	11 (100)	85 (100)
hotstart	4 ( 32)	6 (100)	3 ( 27)	74 ( 86)

Summersmog: mg ethene-equivalent/km				
coldstart	239 (100)	140 (100)	76 (100)	318 (100)
hotstart	101 ( 42)	79 ( 56)	59 ( 78)	281 ( 88)

acidification: mmol H <sup>+</sup> /km				
coldstart	5.2 (100)	3.2 (100)	3.7 (100)	18.0 (100)
hotstart	4.1 (79)	2.1 ( 65)	2.9 ( 79)	17.0 ( 95)

GWP: g CO <sub>2</sub> -equivalent/km				
coldstart	244 (100)	211 (100)	203 (100)	241 (100)
hotstart	218 ( 89)	192 ( 91)	189 ( 93)	222 ( 92)

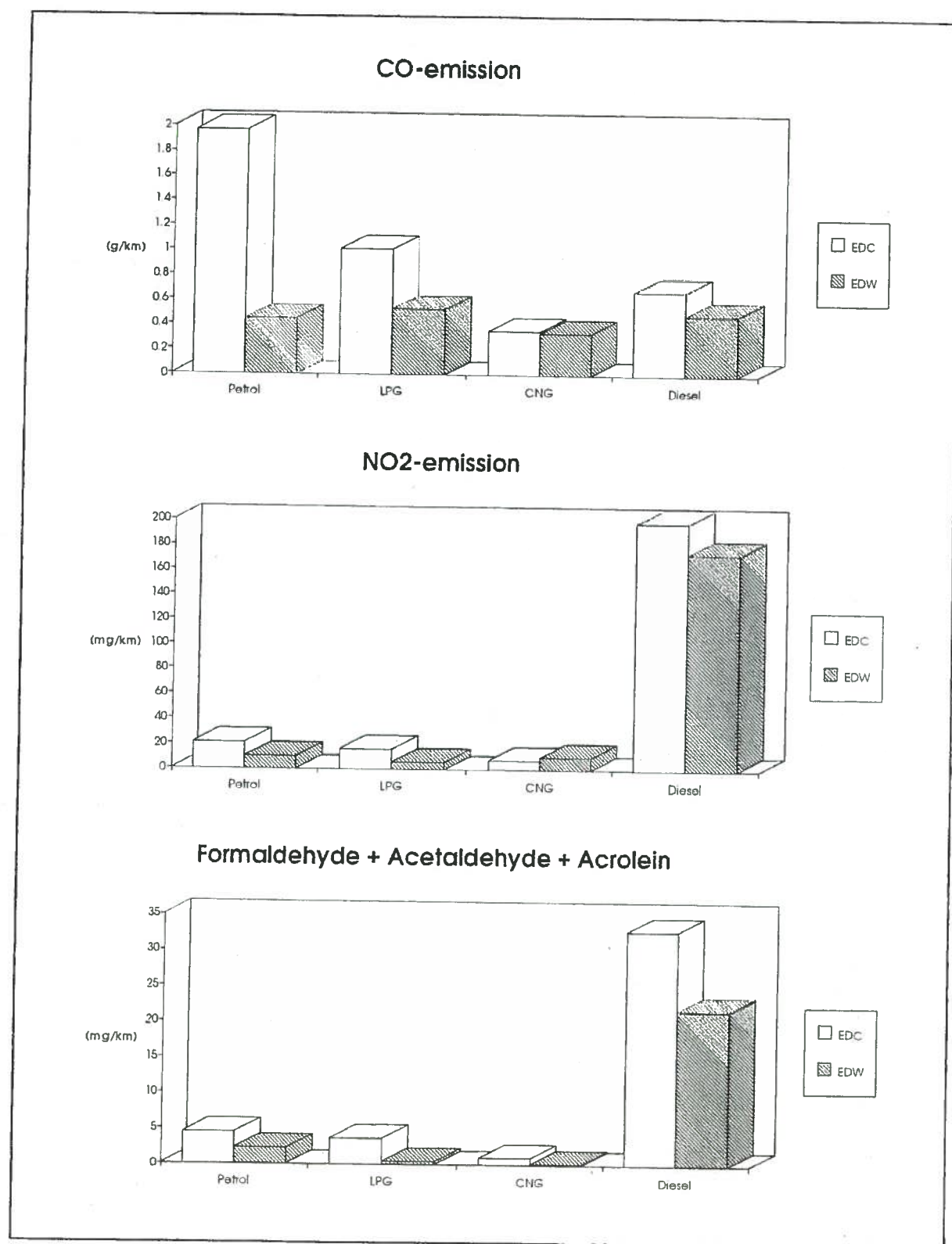


Figure 6.1a: Coldstart effects on direct toxic components



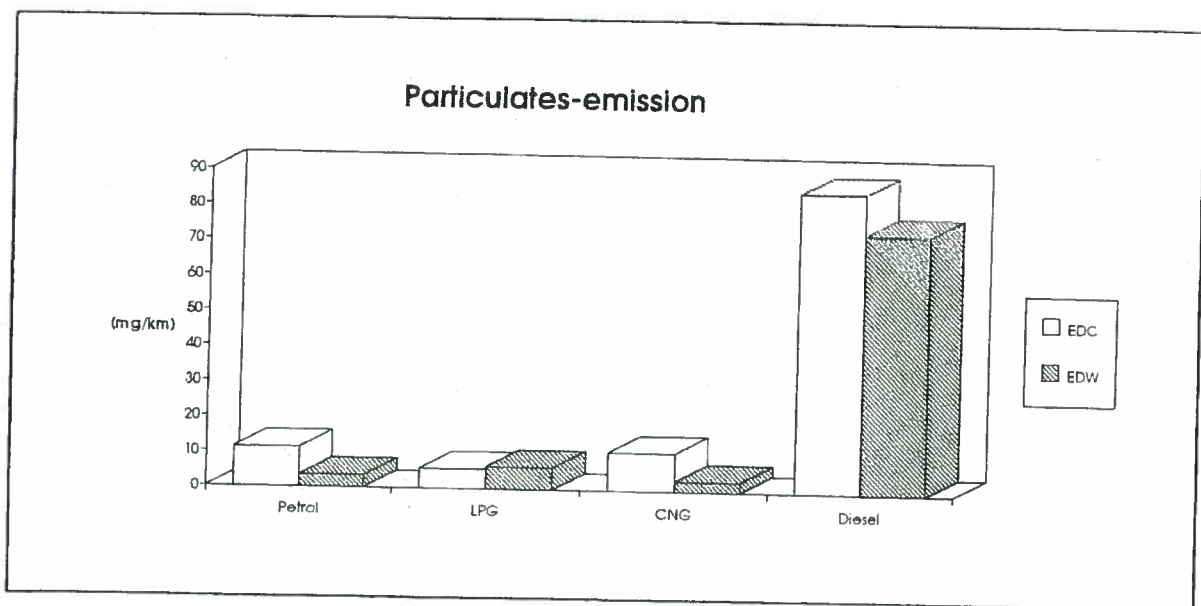


Figure 6.1b: Coldstart effects on direct toxic components (concluded)

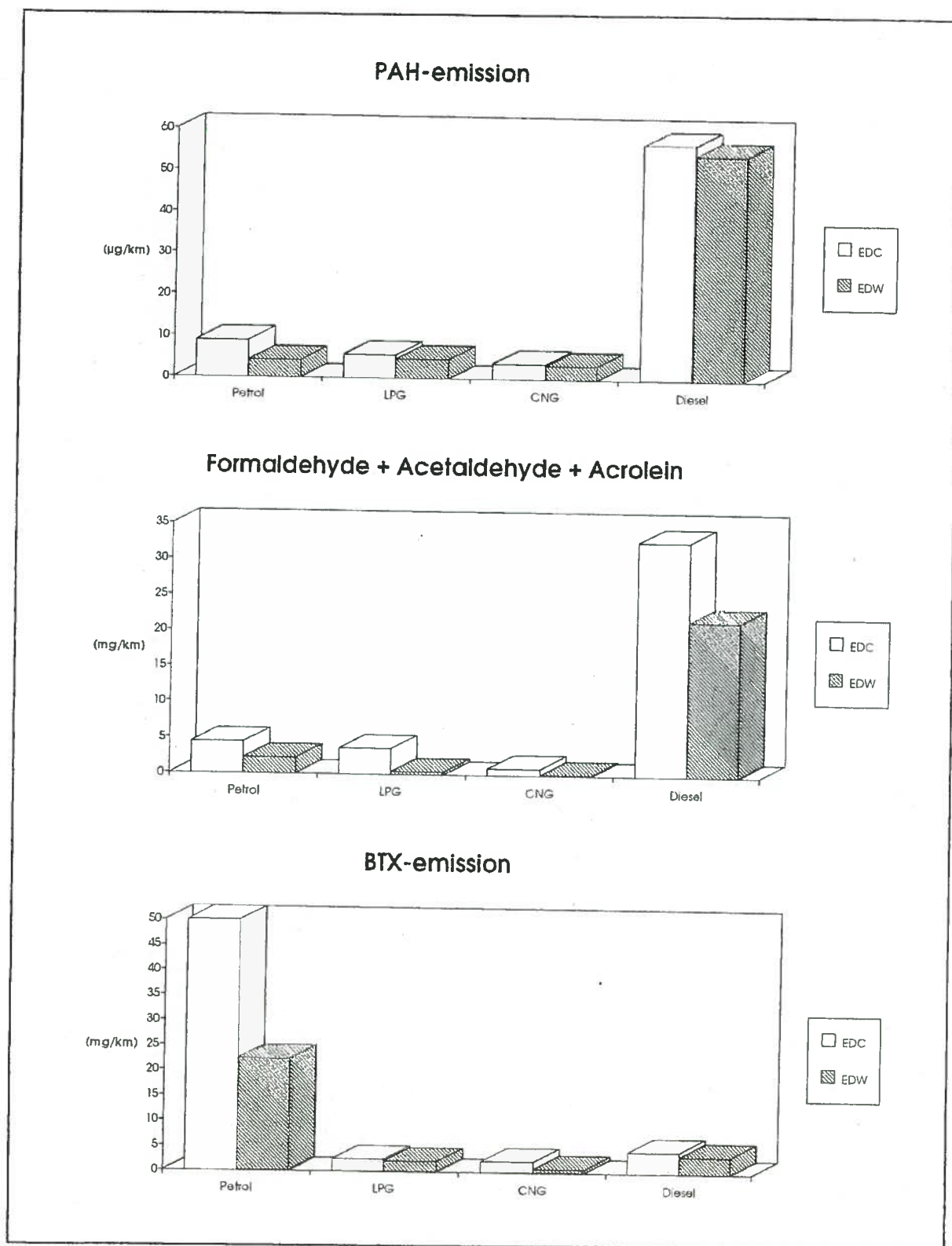


Figure 6.2: Coldstart effects on long-term toxic effects

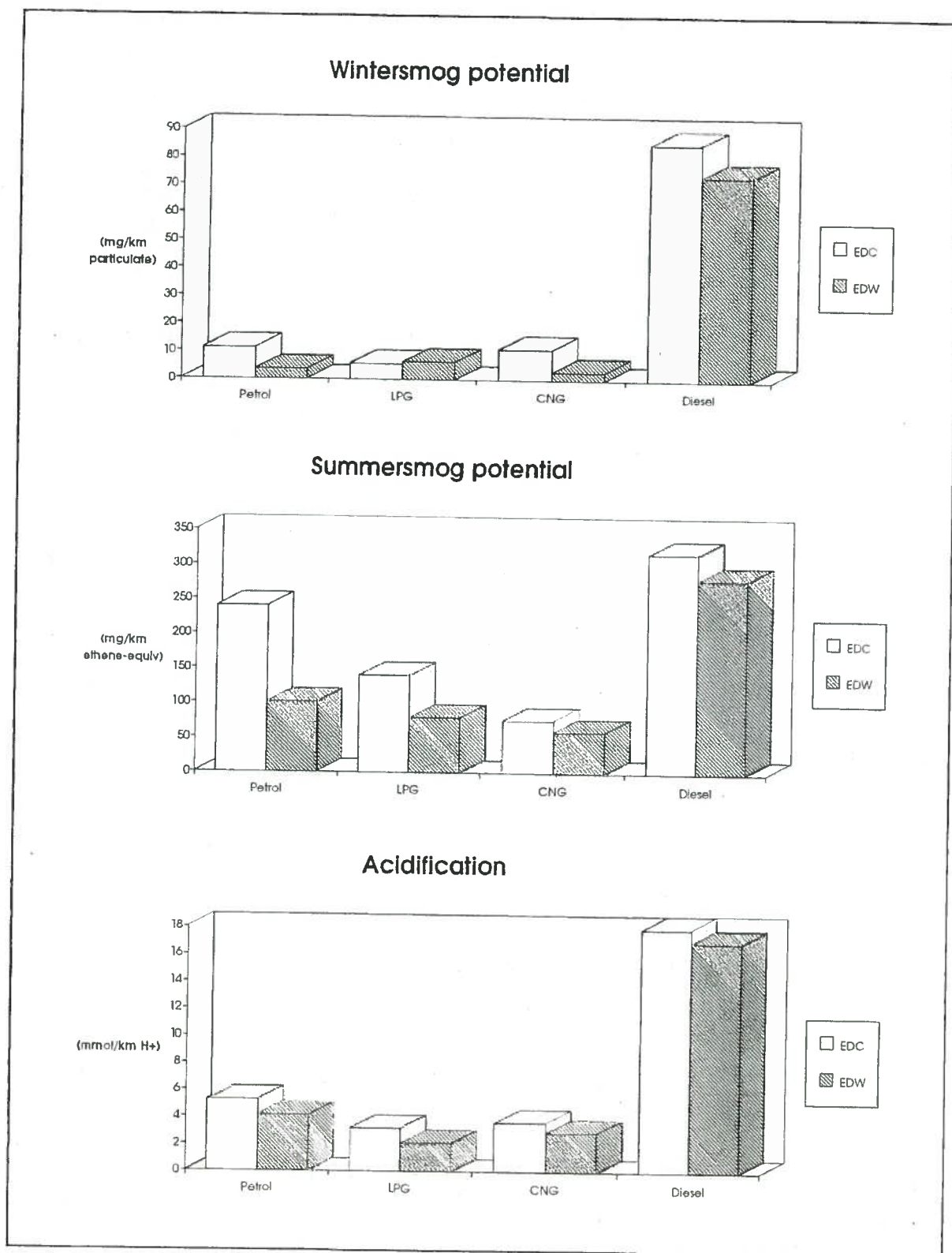


Figure 6.3a: Coldstart effects on regional and global effects

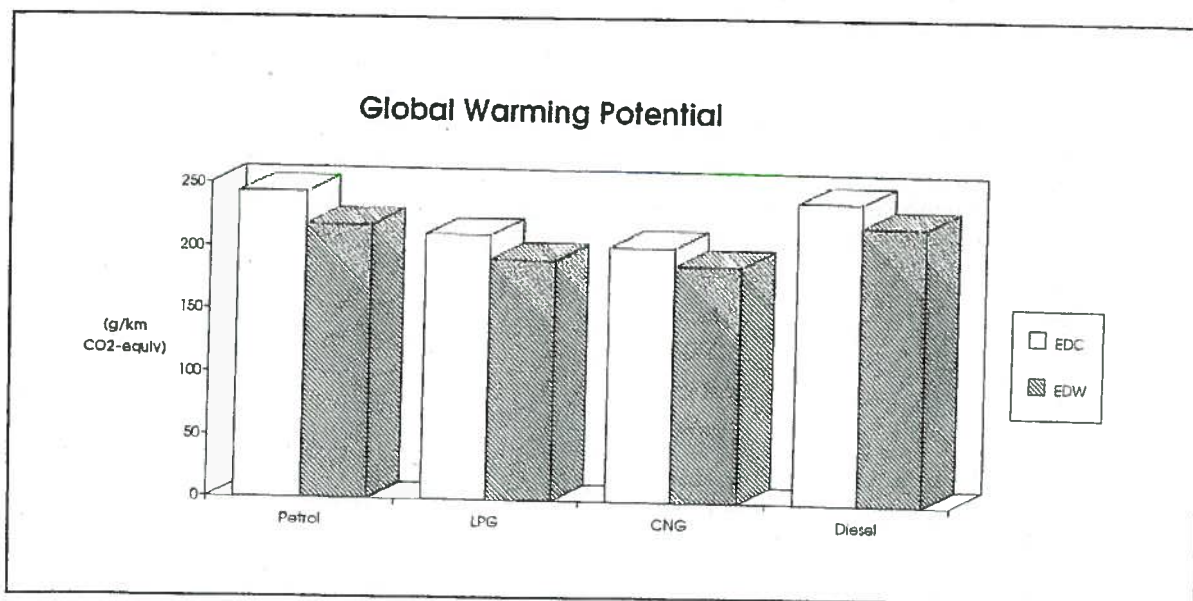


Figure 6.3b: Coldstart effects on regional and global effects (concluded)

## 6.2 Diesel technology

Two of the diesel passenger cars were fitted with conventional engines. The other two were fitted with an oxidation catalyst and a mild degree of turbocharging to increase air/fuel ratio's. These two groups can be compared with each other. The fifth vehicle was fitted with a direct injection diesel engine. But since this vehicle was a light van, comparison with the indirect injection diesel (all passenger cars) was not very well possible. Table 6.4 and Figure 6.4 show the comparison between the conventional and the catalyst fitted cars. In the case of the direct toxic components the gaseous emissions of the catalyst equipped cars are about half that of the conventional cars. The particulate emission, however, is about equal. Of the long-term toxic components, the lower aldehydes are halved, but PAH and BTX remain more or less the same. Of the regional and global effects the summersmog shows a more than marginal decrease with the catalyst fitted; the other effects remain largely unchanged.

These results are somewhat remarkable, since the first reports about the catalysed diesel were that it oxidised the organic compounds, including the heavy hydrocarbons that condense on the particulate fraction; PAH would be halved. In this project the HC-emission is indeed cut by a third but the PAH-

emission is not reduced, nor is the measured particulate emission. In the first reports it was said that the turbocharging aimed at increasing the air/fuel ratio, thereby preventing an increase of  $\text{NO}_x$ . In this project the  $\text{NO}_x$ -emission decreases by about 11% (which is negligible, regarding the spread in results) but the  $\text{NO}_2$  decreases by about 50%. One conclusion from this remarkable effect is that the catalyst does not oxidise large quantities of  $\text{NO}$  into  $\text{NO}_2$ . Nor are hydrocarbons oxidised into aldehydes and ketones, since the overall aldehyde emission is reduced by 55%.

When the different cycles are regarded it appears that for the catalyst equipped diesels the oxidisable components ( $\text{CO}$ ,  $\text{HC}$  aldehydes and  $\text{PAH}$ , and to a smaller extent particulates) are considerably less than those of the conventional diesel, in the US'75 driving cycle and the actual urban driving pattern. Obviously the catalyst is particularly effective in the coldstart cycles. In the warm European driving cycle and the traffic jam condition the particulate emission of the catalyst equipped cars is considerably higher (1.4 and 1.7 times respectively) than that of the conventional cars. In the warm European driving cycle the emission of  $\text{PAH}$  of the catalyst equipped cars also stands out, where as in the traffic jam the  $\text{CO}_2$ -emission of the catalyst equipped cars increases more than that of the conventional cars. The coldstart European driving cycle agrees largely with the weighted average trip (passenger car operation). When comparing the warm European driving cycle with the coldstart European driving cycle, it appears that the emissions of particulates and  $\text{PAH}$ , which are equal for both technologies in the coldstart test, decrease for the conventional cars in the warm test, but not for the catalyst equipped cars.

Table 6.4: Differences between conventional and advanced technology for diesel engines

Direct toxic components		conventional	with turboch. + cat.
CO	g/km	0.71 (100)	0.30 ( 42)
NO <sub>2</sub>	mg/km	198 (100)	111 ( 56)
formaldehyde+	mg/km	33 (100)	16 ( 49)
particulates	mg/km	63 (100)	69 (108)

Long-term toxic effects			
PAH	µg/km	55 (100)	52 ( 94)
Formaldehyde+	mg/km	33 (100)	16 ( 49)
BTX	mg/km	3.1 (100)	3.3 (107)

Regional + global effects			
wintersmog	mg/km	63 (100)	69 (108)
summersmog	mg/km	298 (100)	228 ( 77)
acidification	mg/km	16 (100)	15 ( 90)
GWP	g/km	232 (100)	235 (101)



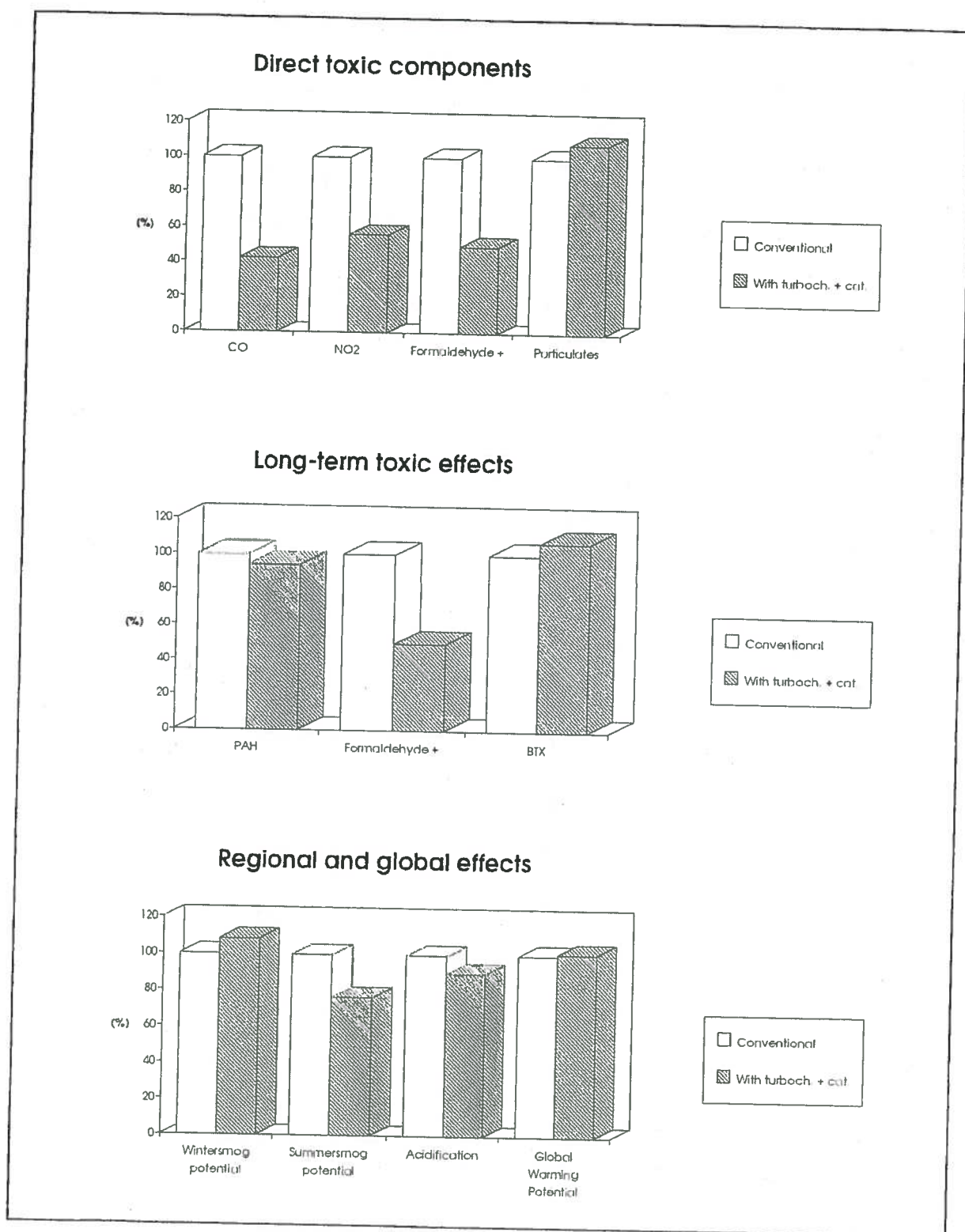


Figure 6.4: Differences between conventional and advanced technology for diesel engines



## 7 INDIRECT AND OTHER NOT MEASURED EMISSIONS

The measured values are all tailpipe emissions. For a complete picture the emissions from oil well exploitation, transport, refining, storage and distribution should be added. Such emissions can be summarised as indirect emissions. Together with the tailpipe emissions they can cause regional or global effects. Yet another category of emissions is the evaporation of petrol from petrol tanks. Although such emissions take place on the vehicle, and could therefore be classified as direct emissions, they are not included in the tailpipe values. In some earlier studies [7], [4] indirect emissions are estimated for the various fuels regarded in this study. The components considered were CO, VOC (Volatile Organic Compounds) largely equivalent to NMHC (Non Methane Hydrocarbons),  $\text{CH}_4$ ,  $\text{NO}_x$ ,  $\text{CO}_2$ ,  $\text{SO}_2$  and particulates. These figures were taken as g of component per kg of fuel burned. Since the fuel burned is known for each test condition, it is possible to calculate an (estimated) indirect emission for each vehicle/fuel/cycle combination. In fact the vehicles and cycles have first been averaged into a passenger car operation figure and a light van operation figure. Since these two in most cases do not differ fundamentally, only the first has been used to judge the indirect effects. These indirect effects have been calculated, as indicated, on the basis of average fuel consumption per fuel.

In the case of summersmog (ethene-equivalent), PAH, BTX and formaldehyde+, where a more detailed emission picture is needed, it was assumed that these effects (or the VOC-related part of the effect) are proportional to the indirect NMHC emissions. To this end the indirect NMHC was calculated as a percentage of the direct NMHC. For the summersmog also an estimate was made of the evaporative emission from fuel tanks. This contribution was set at 2 g/day which works out at approx. 40 mg/km. This contribution was not taken into consideration for the calculation of PAH and formaldehyde+, since it is assumed that most of the direct PAH and aldehydes is formed in the combustion chamber. The evaporative emissions are relevant not only for petrol, but also for LPG and CNG, since these fuels are usually applied in a dual-fuel system, with some petrol in the petrol tank.

In the case of GWP the contributions of indirect  $\text{CO}_2$ , CO,  $\text{CH}_4$ , NMHC and  $\text{NO}_x$  can be calculated as for the direct emissions. An unknown contribution is that of tailpipe  $\text{N}_2\text{O}$ , however. The emissions of  $\text{N}_2\text{O}$  are low, but since this

component has a GWP-factor of 290, the contribution to GWP can still be significant. In the course of the project some  $N_2O$ -measurements were made. On the basis of these measurements the following  $N_2O$ -emissions are estimated:

- \* petrol      average  $N_2O$  = 25 mg/km
- \* LPG        average  $N_2O$  = 15 mg/km
- \* CNG        average  $N_2O$  = 5 mg/km
- \* diesel     average  $N_2O$  = 5 mg/km

The indirect emissions as used for this study are shown in Table 7.1. The upper part of the table gives the indirect emissions in g/kg fuel and the lower part in g (mg)/km. The resulting overall emissions are shown in Tables 7.2 and 7.3 and Figures 7.1 and 7.2. From Table 7.2 and Figure 7.1 (long-term toxic effects) it appears that, especially on PAH and Formaldehyde+, the relative emission from CNG doubles and that from diesel decreases with about a quarter (relative to petrol), but this has little influence on the ranking. Similar effects can be observed for the BTX, but they are of small absolute magnitude, and of small significance due to the dominance of petrol in this group. The accuracy of the figures for CNG depends heavily on the accuracy of the direct and indirect figures for VOC: since the actual NMHC is extremely low for CNG the multiplication factor for NMHC (indirect vs direct) is correspondingly high. That means that a slight variation in the determination the direct emissions has large consequences in the estimate of the indirect emission. Similarly slight departures from the proportionality of PAH, BTX and Formaldehyde+ with NMHC will result in large fluctuations of the indirect figures.

From Table 7.3 and Figure 7.2 the influence of the non-measured emissions on the regional and global effects can be judged. Table 7.3.a. shows that the indirect contribution to wintersmog is about as large as the direct contribution for petrol and LPG. For CNG the indirect contributions is very low indeed, so that the relative total contribution decreases. Also the relative total contribution of diesel decreases (from about 9x to about 5x), but it is still an order of magnitude larger than that of the other fuels. The overall contribution to summersmog is largely uninfluenced by the indirect emissions, except that of diesel, which decreases from 158% to 112% (relative to petrol). As to acidification the relative contribution of CNG and diesel decreases significantly, when one also considers indirect effects, but even so diesel stands out as the most acidifying fuel. In the case of global warming CNG and diesel change in the same proportion; petrol increases the

most and LPG changes in a degree that is about average between petrol on the one hand and CNG or diesel at the other. The result is that petrol is clearly worse than diesel in an overall consideration and that CNG is clearly better than LPG.

Table 7.1: Indirect emissions

Indirect emissions: (g/kg fuel)	CO <sub>2</sub>	CO	VOC (NMHC)	CH <sub>4</sub>	NO <sub>x</sub>	partic.	SO <sub>2</sub>
Petrol	550	1.85	2.10	2.0	1.25	0.13	4.25
LPG	400	1.90	1.10	2.0	1.20	0.12	3.65
CNG	200	0.03	0.50	5.0	0.13	0.00	0.07
diesel	400	1.75	0.70	1.9	1.10	0.11	3.60

Indirect emissions	CO <sub>2</sub> g/km	CO mg/km	VOC (NMHC) mg/km	CH <sub>4</sub> mg/km	NO <sub>x</sub> mg/km	partic. mg/km	SO <sub>2</sub> mg/km
Petrol	38	131	187*	140	88	9.2	300
LPG	25	124	114*	134	78	7.9	240
CNG	18	3	82*	428	11	0.3	6
diesel	25	112	43	122	71	7.0	228

\*plus 40 mg/km evaporative loss

Table 7.2: Long-term toxic effects (indirect emissions estimated from NMHC-contribution)

PAH	direct		indirect	total	
	µg/km	(%)		µg/km	(%)
Petrol	8.9	(100)	7.1	16.1	(100)
LPG	5.5	( 62)	3.8	9.3	( 58)
CNG	4.1	( 46)	9.0	13.1	( 81)
Diesel	62	(700)	24	86	(530)

BTX	direct		indirect	total	
	mg/km	(%)		mg/km	(%)
Petrol	42	(100)	33	75	(100)
LPG	2.9	( 7)	2.0	4.9	( 7)
CNG	2.0	( 5)	4.3	6.3	( 8)
Diesel	3.9	( 9)	1.5	5.5	( 7)

Lower aldehydes	direct		indirect	total	
	mg/km	(%)		mg/km	(%)
Petrol	3.4	(100)	2.7	6.1	(100)
LPG	2.4	( 71)	1.6	4.0	( 66)
CNG	0.6	( 18)	1.4	2.0	( 33)
Diesel	29	(860)	11	41	(670)

Table 7.3: Regional and global effects

Wintersmog (particulates)	direct		indirect mg/km	total	
	mg/km	(%)		mg/km	(%)
Petrol	9.5	(100)	9.2	18.7	(100)
LPG	5.8	( 61)	7.9	13.7	( 73)
CNG	10.6	(112)	0.34	11.0	( 59)
diesel	84	(880)	7	91	(490)

a

Summersmog (ethene-equivalent)	direct		indirect (%)	total	
	mg/km	(%)		mg/km	(%)
Petrol	193	(100)	120	313	(100)
LPG	129	( 67)	81	210	( 67)
CNG	70	( 36)	36	106	( 34)
diesel	305	(158)	46	351	(112)

b

Acidification (H <sup>+</sup> )	direct		indirect mmol/km	total	
	mmol	(%)		mmol/km	(%)
Petrol	4.9	(100)	11.3	16.2	(100)
LPG	3.2	( 65)	9.2	12.5	( 77)
CNG	3.3	( 67)	0.4	3.7	( 23)
diesel	17.6	(360)	8.7	26.3	(162)

c

GWP (CO <sub>2</sub> -equivalent)	direct		N <sub>2</sub> O (estim) g/km	indirect g/km	total	
	g/km	(%)			g/km	(%)
Petrol	239	(100)	7.3	47	293	(100)
LPG	209	( 87)	4.4	33	246	( 84)
CNG	202	( 85)	1.5	28	232	( 79)
diesel	236	( 99)	1.5	31	269	( 92)

d

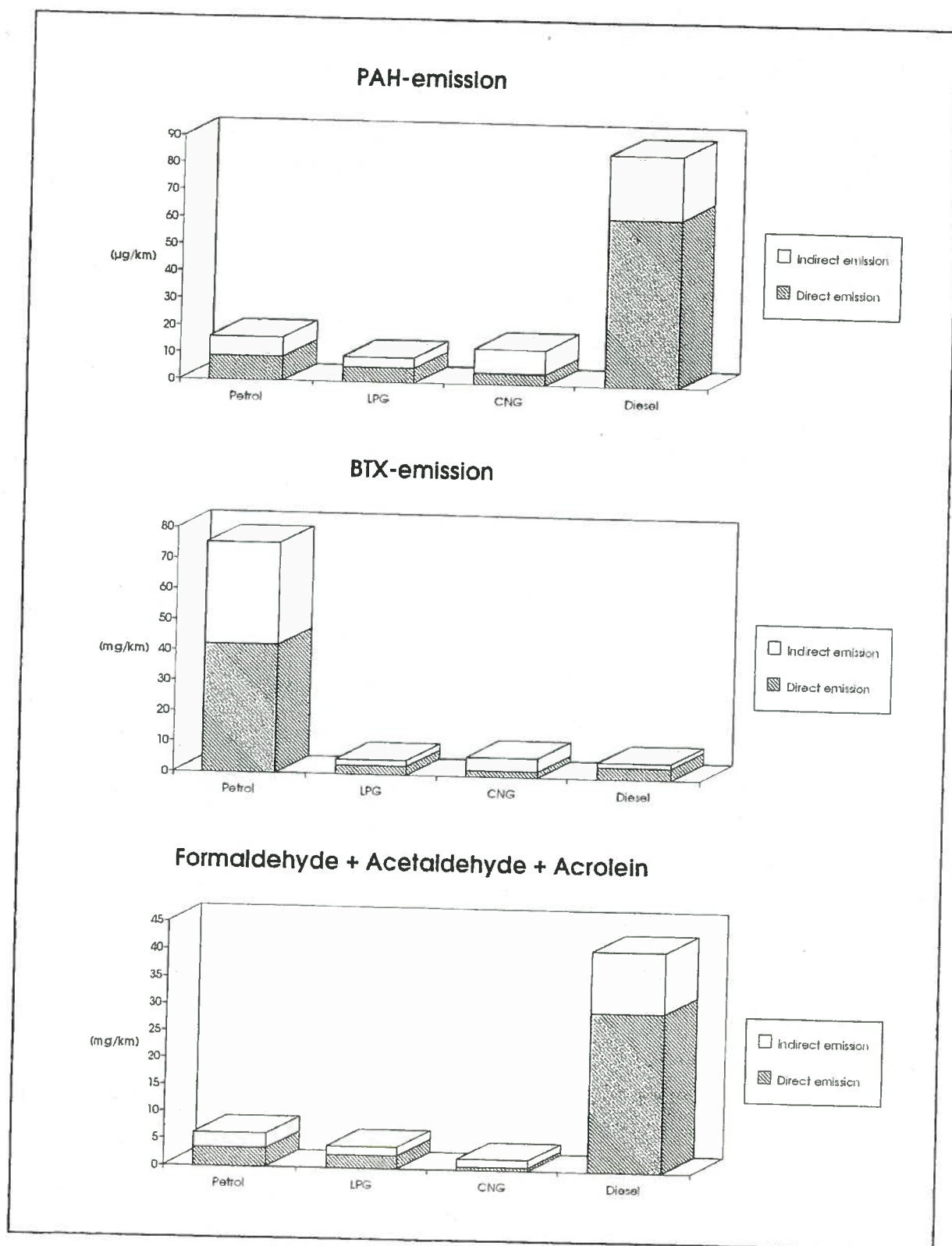


Figure 7.1: Long-term toxic effects



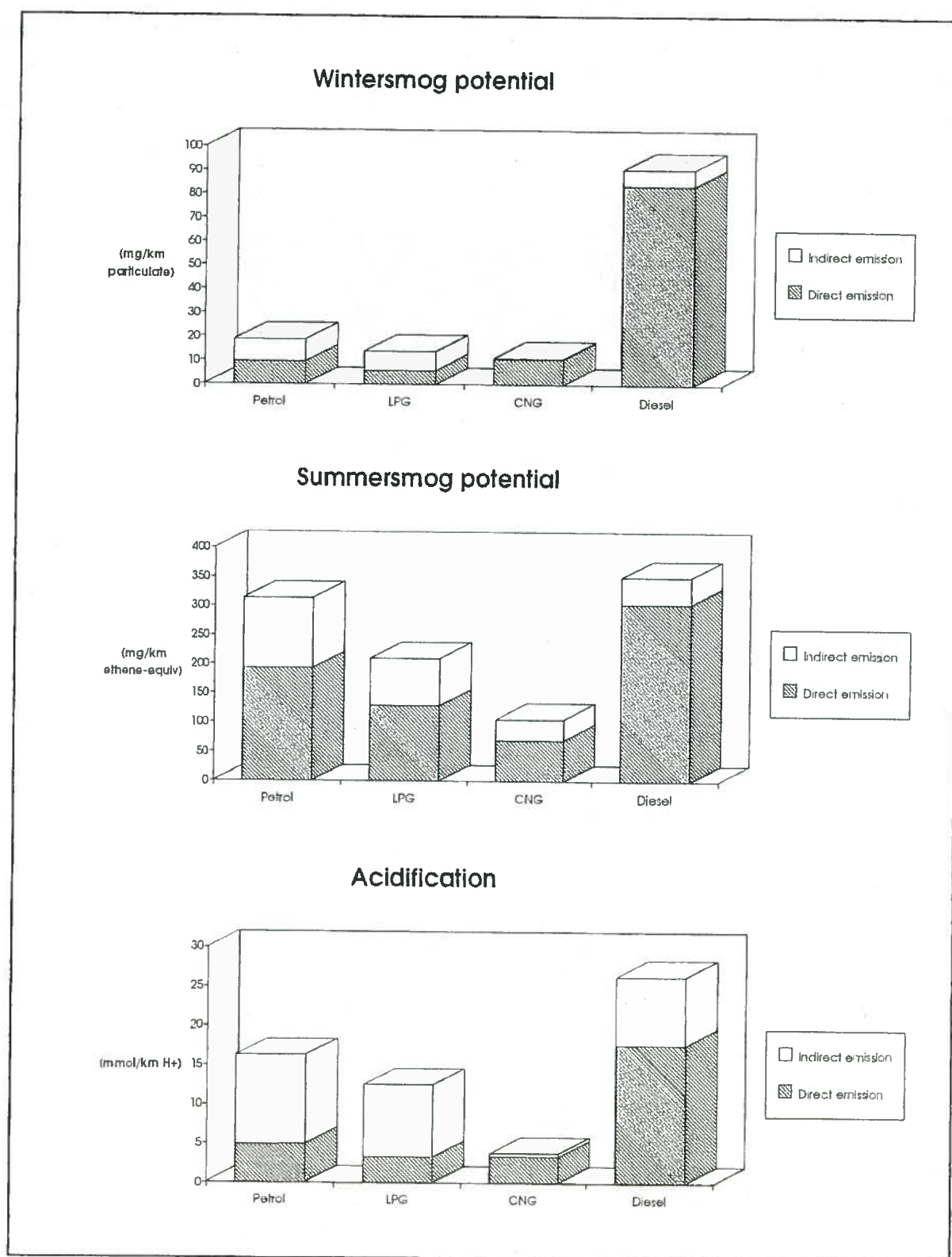


Figure 7.2a: Regional and global effects



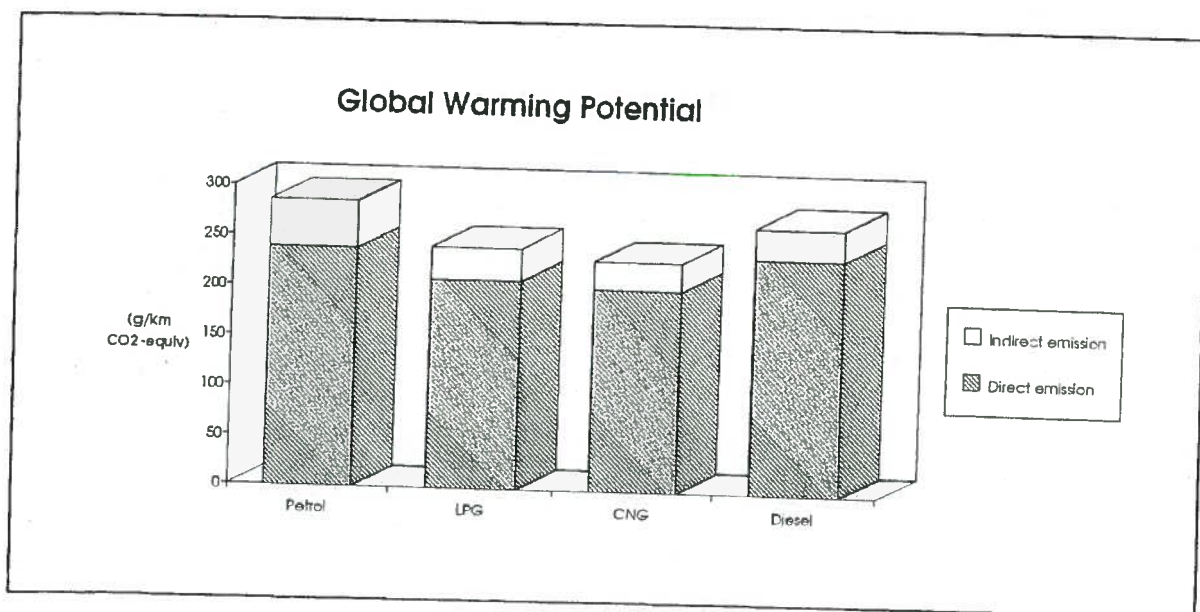


Figure 7.2b: Regional and global effects (concluded)

## 8 STATISTICAL CONSIDERATIONS

### 8.1 Statistical significance of the overall differences

The emission values averaged per fuel have an accuracy that is limited due to the sometimes large spread between the five vehicles per fuel. In the case of CNG the uncertainty is further enhanced by the fact that only two vehicles have been measured. One may then well ask what is the significance of the differences between the fuels. In order to shed some light on this, a (two-sided) Student-t check has been made on each relevant pair of datasets. As a rule a 95% confidence level has been chosen. This leads to the following conclusions:

#### **Direct toxic effects**

In the case of CO only petrol shows a significant trend on the high side in some cycles (mainly the actual urban driving pattern) and CNG on the low side (mainly in the coldstart European driving cycle and the traffic jam). See Fig. 8.1.

In the case of NO<sub>2</sub> the diesel vehicles show a consistent significant trend on the high side relative to all other fuels. The CNG fuel shows an additional significant trend on the low side relative to petrol and/or LPG in the coldstart cycles. See Fig. 8.2.

In the case of the lower aldehydes the diesel differs significantly from all other fuels in all cycles and the CNG from all other fuels in the coldstart cycles. That means that in the coldstart cycles only the relation petrol-LPG shows no significant difference. In the hot cycles (warm European driving cycle and actual traffic jam pattern) there is no significant difference between the spark ignition fuels amongst each other at the 95% confidence level, but sometimes there is at the 90% confidence level. See Fig. 8.3.

In the case of particulates there is a consistent significant trend on the high side between diesel and all other fuels, but with some exceptions no significant trend between the other fuels mutually. See Fig. 8.4.

So to summarise: diesel fuel consistently scores high in a significant way while of the other fuels CNG often scores low in a significant way, especial-

ly in the coldstart cycles. There is usually no significant difference between petrol and LPG, mainly due to the high spread in the petrol results.

#### **Long-term toxic effects**

With regard to PAH the diesel engines scores significantly high relative to the other fuels. The other fuels do not show statistically significant differences amongst each other, due to the high spread in the petrol results and the low number of CNG-vehicles. With the addition of the indirect emissions the emissions on LPG are significantly lower than those on petrol and CNG at the 90% confidence level; there is then still no significant difference between petrol and CNG. See Fig. 8.5.

With regard to the lower aldehydes only the relation petrol-LPG is not significant, due to a small difference between the mean values. All other relations are statistically significant at the 95% confidence level. This situation does not change when the indirect emissions are taken into account. See Fig. 8.5.

With regard to the BTX-group the petrol results are significantly higher than those on the other fuels at the 90% confidence level, but not at the 95% confidence level due to the high spread in the petrol results. The other fuels do not significantly differ mutually. When the indirect effects are taken into account the difference between petrol and the other fuels becomes significant at the 95% confidence level. The other pairings, however, still are not significant. See Fig. 8.5.

So it can be said that the diesel scores significantly high in PAH and formaldehyde+, CNG scores low in formaldehyde+ and petrol scores high in BTX.

#### **Regional and global effects**

Wintersmog is in this study related to particulate emission. On particulates the diesel scores significantly higher than all other fuels, but mutually the other fuels do not differ in a significant way. This situation does not change when indirect emissions are taken into account. See Fig. 8.6.

With regard to summersmog the difference between petrol and LPG is not significant due to the high spread in the petrol results. The differences between the other pairings are significant at the 90% confidence level (petrol-diesel and LPG-CNG) or at the 95% confidence level. When the indirect emissions are added the difference between petrol and diesel becomes insig-

nificant, those between petrol and either of the gaseous fuels becomes significant at the 90% confidence level, and all others become or remain significant at the 95% confidence level. See Fig. 8.6.

With regard to acidification all differences are significant at the 95% confidence level, except those between CNG on the one hand and petrol and LPG on the other. When indirect effects are taken into account these two become significant as well, due to the low indirect contribution in the case of CNG. See Fig. 8.6.

With regard to global warming the differences between either of the liquid fuels on the one hand and either of the gaseous fuels on the other are all significant at the 95% confidence level. The differences between both the liquid fuels and between both the gaseous fuels are not significant. When an estimated contribution of  $N_2O$  plus the indirect emissions are taken into account the difference between petrol and diesel becomes significant at the 90% confidence level. The difference between LPG and CNG remains insignificant. The other relations remain significant at the 95% confidence level. See Fig. 8.6.

	D	C	L	P		D	C	L	P
P	-	+	-		P	-	-	-	
L	-	+			L	-	-		
C	-				C	-			
D					D				
EDC					EDW				
	D	C	L	P		D	C	L	P
P	-	-	-		P	+	+	+	
L	-	-			L	-	-		
C	-				C	-			
D					D				
US					City				
	D	C	L	P		D	C	L	P
P	-	-	-						
L	-	+							
C	+								
D									
Jam									

+ stat. significant at 95% confid. level  
o stat. significant at 90% confid. level  
- stat. not significant

Figure 8.1: Statistical significance of comparisons between fuel-pairs: CO

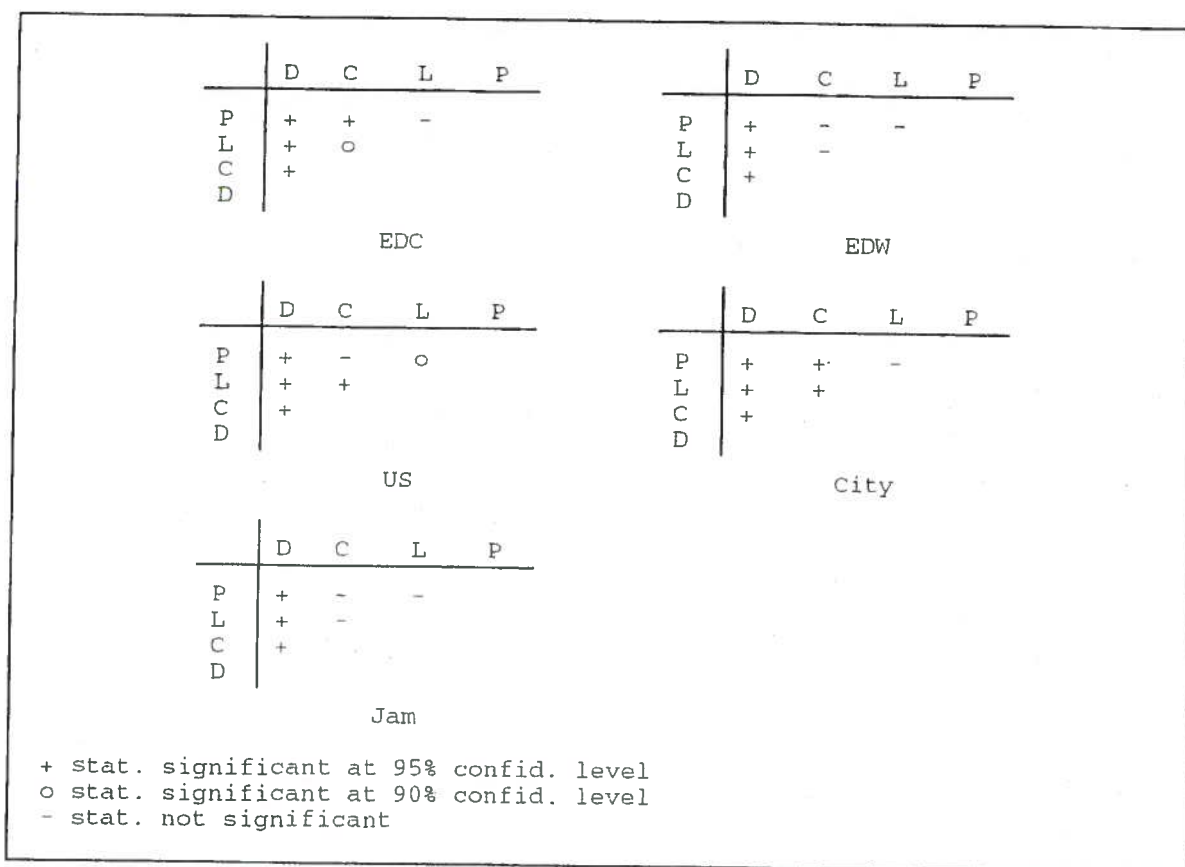


Figure 8.2: Statistical significance of comparisons between fuel-pairs: NO<sub>2</sub>

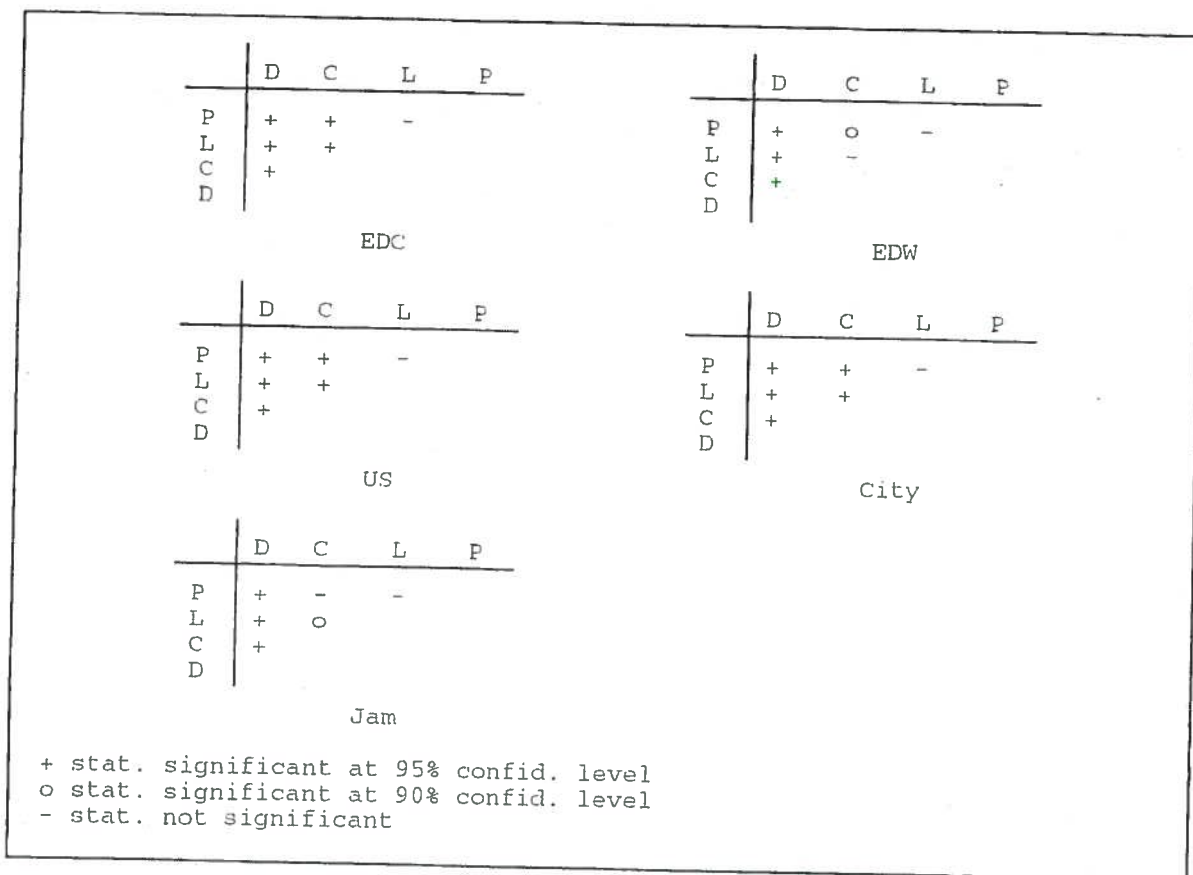


Figure 8.3: Statistical significance of comparisons between fuel-pairs: lower aldehydes



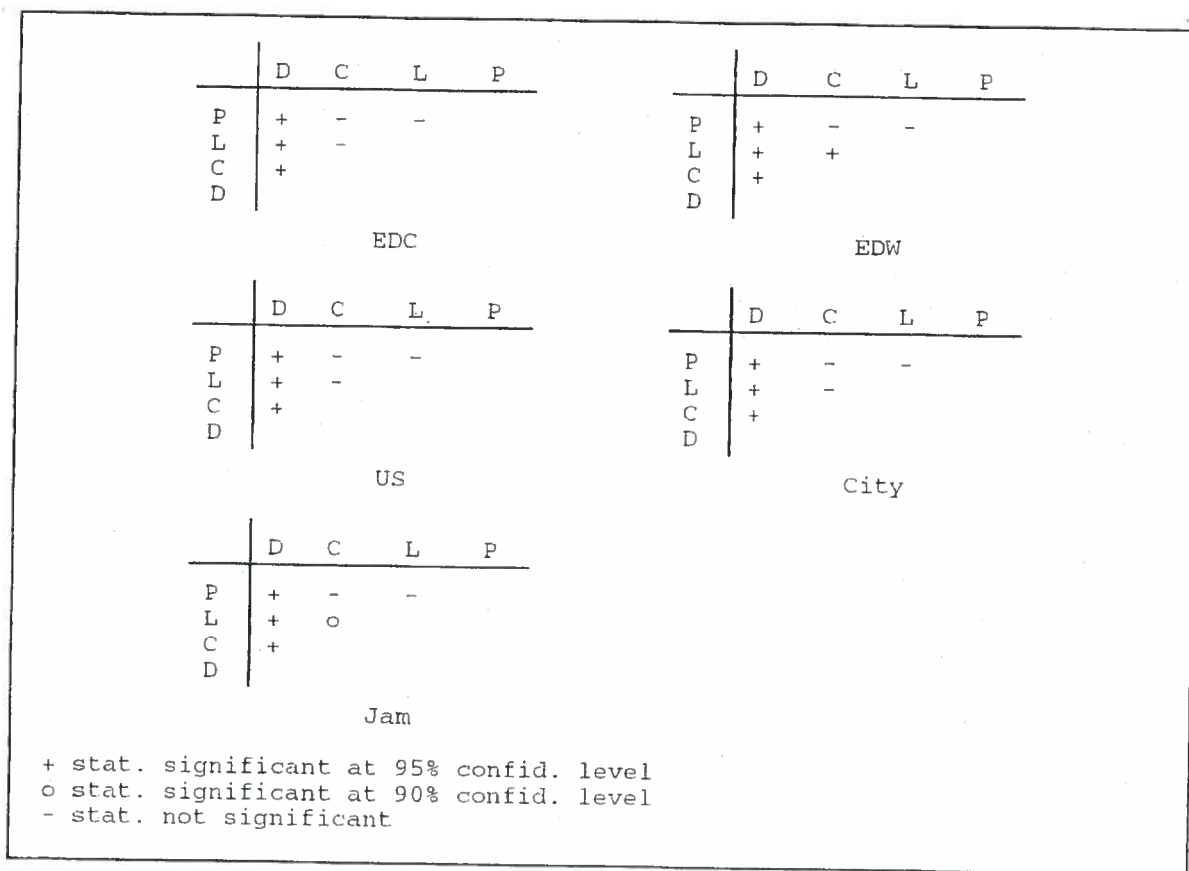


Figure 8.4: Statistical significance of comparisons between fuel-pairs: particulates

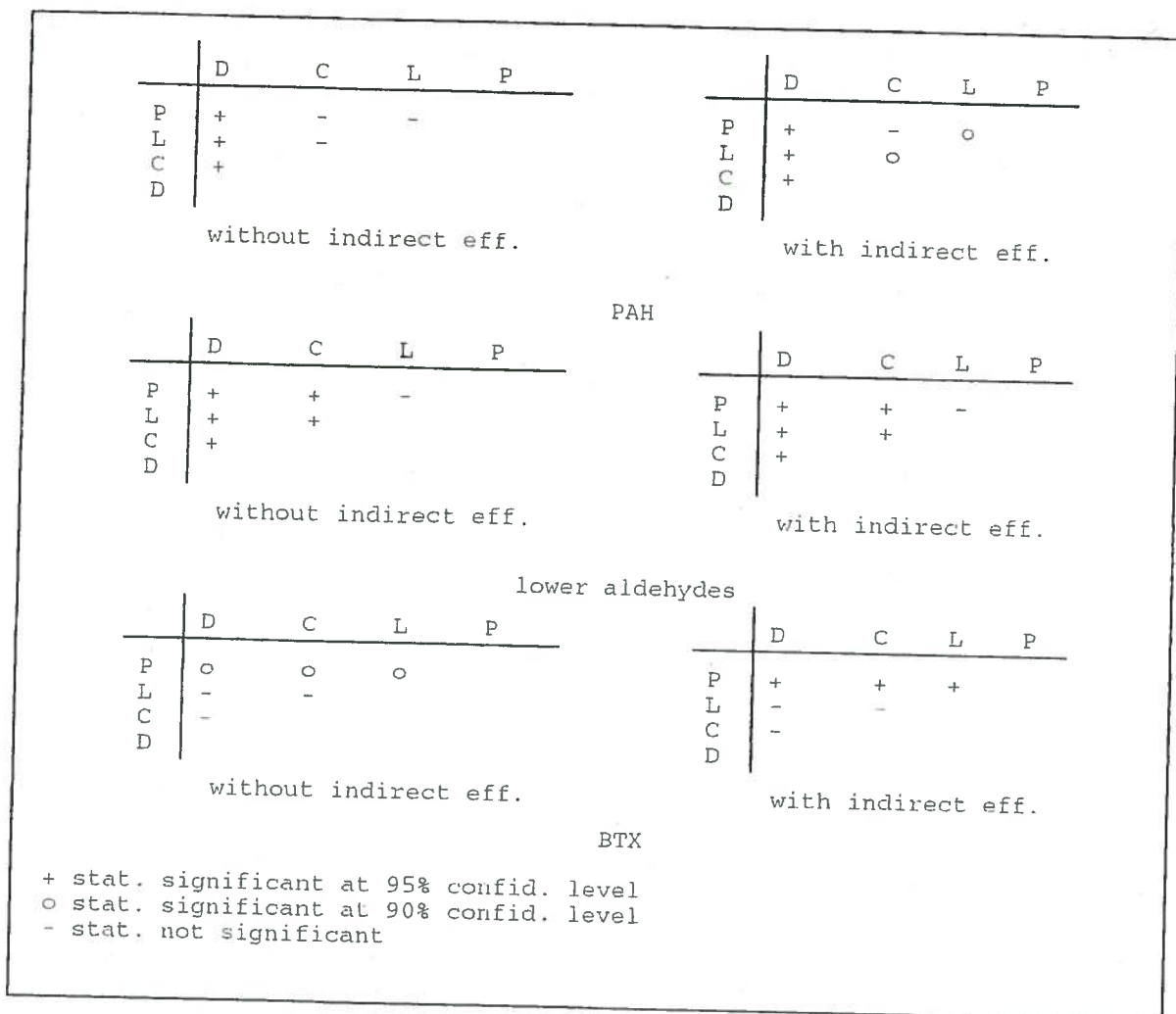


Figure 8.5: Statistical significance of comparisons between fuel-pairs: long-term toxic effects

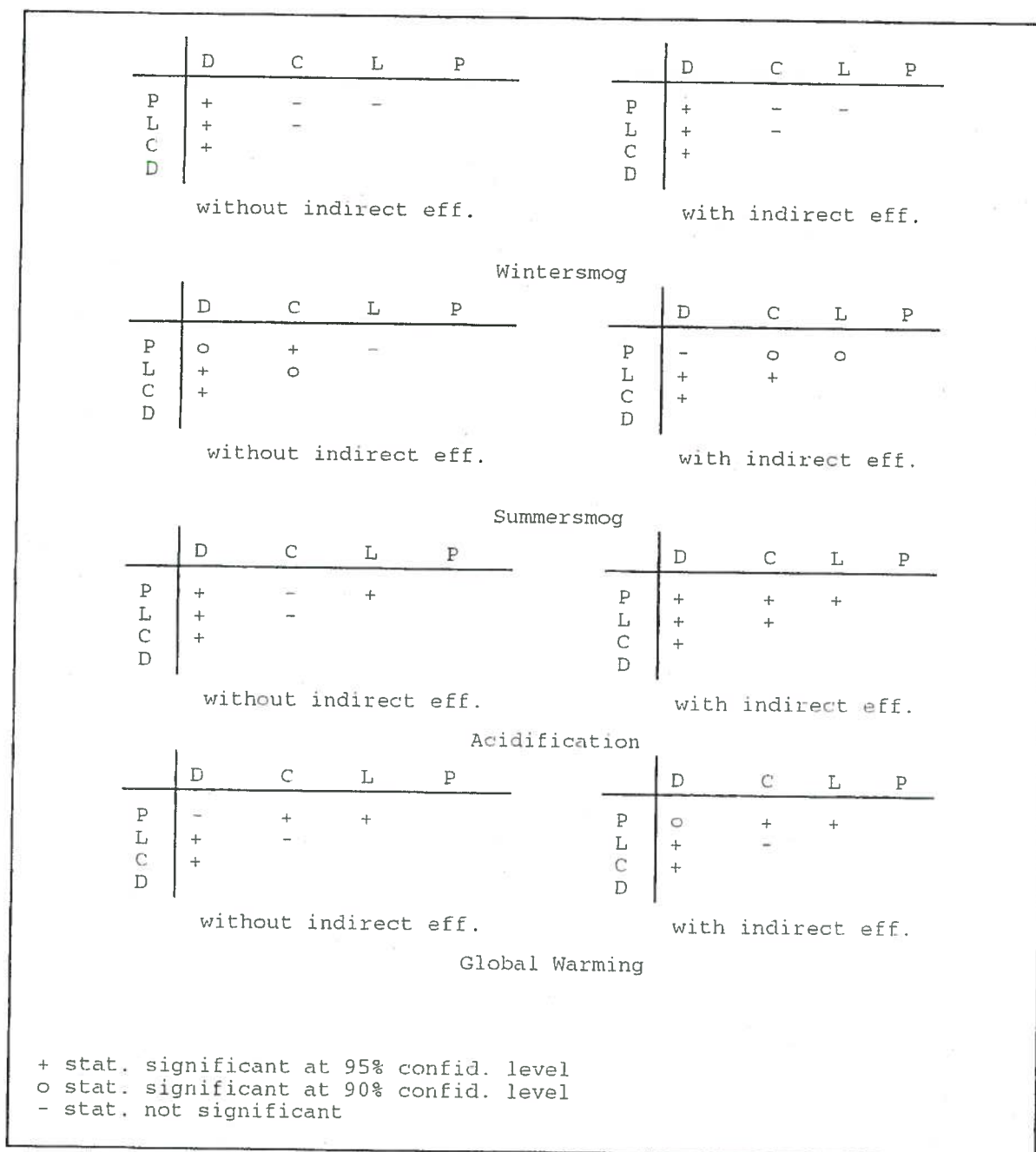


Figure 8.6: Statistical significance of comparisons between fuel-pairs: regional and global effects

## 8.2 Repeatability of the testing

The coldstart European driving cycle and the urban driving pattern (also coldstart) have been measured in duplicate because coldstart tests usually have a poorer repeatability than hotstart test; by performing them in duplicate a more accurate result was expected. In all the previous calculations the mean of the two test results has been used for these two cycles. Yet the fact that these tests were performed twice provides some insight into the repeatability of the testing.

In Table 8.1 - 8.3 the repeatability is shown as half the difference (quasi a standard deviation), both absolute and as a percentage of the mean, for all the environmental effects considered. Table 8.1 shows the results for the direct toxic effects. The repeatability of the CO is good. That of the other components varies according to the actual values measured. Especially the CNG vehicles show a large variance, but at the same sort of absolute level as the other fuels. So the large variance is obviously caused by the low absolute level of the emission. The repeatability of the particulate measurement is poor except for the diesel vehicles (which have a much higher absolute level). This is partly for the same reason, and partly because the repeatability of the particulates measurement is usually poor even under the best of circumstances.

Table 8.2 shows the repeatability of the long-term toxic effects. Again the repeatability is good when the emissions are relatively large, but much poorer when the absolute emissions are low.

Table 8.3 shows the repeatability of the regional and global effects. With the exception of wintersmog (shown as particulate emission!) the repeatability is good. This is all the more striking since the repeatability of the various components contributing to a certain environmental effect is usually less good. Obviously some levelling out takes place in the integrated effects. The repeatability of the GWP is extremely good: usually better than 1% and 2-3 g/km.

Since these are only coldstart tests the average repeatability of all the tests can be regarded as better than shown here.

Table 8.1: Repeatability of the direct toxic components in the two coldstart cycles

	Petrol EDC/city	LPG EDC/city	CNG EDC/city	diesel EDC/city
CO %	8/2	3/1	1/5	1/3
g/km	0.16/0.06	0.02/0.02	0.01/0.04	0.01/0.02
NO <sub>2</sub> %	5/2	14/9	33/0	3/2
mg/km	1/1.5	2.5/5	2.5/0	6.5/5
Ald+ %	20/6	6/7	41/16	2/0
mg/km	0.8/0.2	0.15/0.15	0.35/0.2	0.6/0.1
Partic. %	27/29	20/9	82/48	1/2
mg/km	3.5/2.5	1/0	9/5.5	1/2.5

Table 8.2: Repeatability of the long-term toxic components in the two coldstart cycles

	Petrol EDC/city	LPG EDC/city	CNG EDC/city	diesel EDC/city
PAH %	16/0	17/9	58/28	6/5
µg/km	1.7/0.05	0.9/0.5	2.2/1.7	3.5/4.4
Ald.+ %	20/6	6/7	41/16	2/0
mg/km	0.8/0.2	0.15/0.15	0.35/0.2	0.6/0.1
BTX %	3/0	7/5	13/11	0/3
mg/km	1.2/0.3	0.1/0.2	0.25/0.8	0/0.15

Table 8.3: Repeatability of the regional and global effects in the two cold-start cycles

	Petrol EDC/city	LPG EDC/city	CNG EDC/city	diesel EDC/city
Wint.smog %	27/29	20/9	82/48	1/2
µg/km	3.5/2.5	1/0	9/5.5	1/2.5
Sum.smog %	9/0	6/3	5/1	1/0
mg/km	20/0.5	7.5/6	3.5/0.5	3/0.5
Acid. %	6/0	3/1	6/9	2/1
mmol/km	0.32/0.02	0.11/0.04	0.22/0.27	0.31/0.09
GWP %	1/1	1/1	1/2	1/1
g/km	1/2	2/3	1/4	2/2

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The references 2, 3 and 6 actually form one report together with the present report.



